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CATALOG OF INFRARED ABSORPTION SPECTRA FOR THE IDENTIFICATION OF CHEMICAL FINISHING AGENTS FROM TEXTILES, PART 1

ARS-S-47
October 1974

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CATALOG OF INFRARED ABSORPTION SPECTRA FOR THE IDENTIFICATION OF CHEMICAL FINISHING AGENTS FROM TEXTILES, PART 1

By Robert T. O'Connor,* Elizabeth R. McCall, Nancy M. Morris, and Verne W. Tripp¹

INTRODUCTION

Most fabrics on the market have been treated with one or more chemical finishing agents. These may be processing aids and hand builders, such as mineral or vegetable oils, starches, and sizes, or chemical finishing agents that impart to fabrics such properties as wrinkle recovery, fire retardancy, and resistance to water, oil, and stains.

The ever-increasing use of finishing agents, old and new, has brought with it the problem of identification. Skinkle (10)² appears to have been the first to recognize the need for a systematic analytical procedure to identify chemical finishing agents. In 1946 he suggested a scheme to separate them by extraction with a series of solvents applied in order of increasing polarity. The solubility of a finishing agent in any specific solvent would be an indication of the general type of agent. Lack of any soluble fraction in a given solvent would be clear evidence that finishing agents of the specific type were not present in the analytical sample under examination. Specific identification and final confirmation could be obtained only after subsequent investigation of the materials dissolved in any step of the procedure.

A few years later, Krammes and Maresh (5) proposed modifications to Skinkle's solvent extraction scheme. They utilized microscopy, physical data such as refractive indices, and chemical spot tests and color reactions for final identification or confirmation of a specific chemical finishing agent. These solvent extraction schemes

became the basis for the American Association of Textile Chemists and Colorists AATCC Test Method 94-1973 (1). These proposals place the identification of chemical finishes on a sounder basis, but it cannot be said that a completely systematic analytical procedure for the identification of any chemical finishing agent as yet exists. One major difficulty in developing a scheme of identification is the continual introduction of new chemical finishing agents and the abandonment of older ones. The only practical solution to this problem is constant revision of analytical procedures and continuing analysis of finishing agents.

Infrared spectroscopy provides a reliable method of identifying compounds by "fingerprint" comparison of their spectra. The spectra included in this publication begin a library of the required spectral "fingerprints." They are the infrared absorption spectra of 31 chemical finishing agents removed from cotton fabric. The catalog will be expanded as analyses are made.

It has been clearly demonstrated that identification of a finishing agent by means of infrared absorption spectra requires a library in which each spectrum has been prepared from a known authentic sample of the pure finishing agent after it has been padded onto fabric, cured, and subsequently extracted by the solvent extraction procedure. Libraries of spectra for "fingerprint" comparisons have been prepared for the qualitative identification of coating materials for the paint industry (4) and for the analysis of surface-active agents used in the detergent industry (3). By cooperation among industry and research organizations, similar libraries of finishing agents can be compiled for the textile industry to make their identification feasible, rapid, and reliable.

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² Italic numbers in parentheses refer to items in "Literature Cited" at the end of this publication.

INFRARED ABSORPTION SPECTRA OF TRICHLOROETHYLENE-SOLUBLE CHEMICAL FINISHING AGENTS

The first group of 26 spectra represents a class of chemical finishing agents soluble in trichloroethylene. These additives were extracted by heating 3- by 4-inch swatches of fabric with approximately 30 ml of freshly distilled trichloroethylene (analytical reagent grade, bp 87.1° C, distilled once through a 15-cm fractionating column to remove the nonvolatile stabilizer) for 15 to 20 minutes on a steam bath. The extract was filtered into a casserole through glass wool. This extraction procedure was repeated on the same piece of fabric, and the second extract was combined with the first. The solution was concentrated on the steam bath, and the final drops of the concentrate were transferred to a clean potassium bromide plate. After the remaining solvent had evaporated, the infrared spectrum was obtained. To insure complete removal of all trichloroethylene-soluble additives that might interfere with subsequent identification of cross-linking reagents, the fabric was extracted with two additional portions of trichloroethylene.

These spectra are presented in pairs: the spectrum of the chemical agent as obtained and the spectrum of the individual finishing agent after padding, curing, and subsequent removal from the fabric. Spectra of the pure reagents were prepared from the aqueous emulsions, as received, by coating an Irtran 2 plate with the emulsion, allowing the plate to dry, and recording the spectrum. It should be noted, in comparing spectra of films cast on Irtran with those on KBr plates, that absorption bands just above 700 cm^{-1} may be slightly less well defined on Irtran than on KBr because Irtran becomes opaque to infrared radiation in the longer wavelength region. All absorptions below 700 cm^{-1} in the spectra of the films on Irtran are due to the Irtran itself. Occasionally, a chemical finishing agent may be padded onto a fabric, undergo heat

curing, and subsequently be removed from the fabric without change in molecular structure and consequent changes in physical and, particularly, optical properties. This is illustrated by the spectra of polyoxyethylene sorbitan monopalmitate (spectra 523 and 524) and of polyurethane (spectra 515 and 516) where the spectrum of the pure reagent from the bottle appears almost identical to that of the trichloroethylene extract from the fabric. However, this similarity is the exception rather than the rule.

The differences in some of these spectra are summarized below; a more detailed analysis has been published (7). The solvent extraction procedure recommended is a separation scheme, and the spectrum of a finishing agent after extraction may appear much simpler than the spectrum of the reagent as supplied. This is illustrated by spectra of the polyolefin finishes as received (508, 510, 512, and 514) compared with the spectra of these materials after padding onto and removal from fabric (507, 509, 511, and 513). The differences in these pairs of spectra arise from the presence of emulsifiers in the reagent from the bottle. A similar separation into polyolefin and emulsifier fractions was observed when the reagent from the bottle was passed through a silica gel column (7).

The condition of the substrate fabric complicates identification of the finishing agent. For example, the doublet at 728 and 718 cm^{-1} in the spectrum of the extract of the polyurethane-treated fabric (spectrum 515) is missing from the spectrum of the polyurethane as received (spectrum 516). This doublet is present in the spectrum of the extract of the substrate fabric and is probably due to a lubricant used in the preparation of the fabric.

The 13 chemical finishing agents soluble in trichloroethylene are listed below by generic classification. The spectra follow the list.

LONG-CHAIN QUATERNARY
AMMONIUM COMPOUNDS

501	Arquad 2HT-75 extracted from treated fabric	KBr
502	Arquad 2HT-75 as received	Irtran
503	Viva Fibreactant extracted from treated fabric	KBr
504	Viva Fibreactant as received	Irtran
505	P and G Finish #4 extracted from treated fabric	KBr
506	P and G Finish #4 as received	Irtran

POLYETHYLENE

507	Polymul CS-81 extracted from treated fabric	KBr
508	Polymul CS-81 as received	Irtran
509	Cellusoft PXB extracted from treated fabric	KBr
510	Cellusoft PXB as received	Irtran

POLYETHYLENE-POLYPROPYLENE MIXTURE

511	Velvetol OE extracted from treated fabric	KBr
512	Velvetol OE as received	Irtran

POLYETHYLENE GLYCOL

513	Carbowax 600 extracted from treated fabric	KBr
514	Carbowax 600 as received	Irtran

POLYURETHANE

515	E-503 extracted from treated fabric	KBr
516	E-503 as received	Irtran
517	X-1015 extracted from treated fabric (CHCl ₃ -acetone fraction from silica gel column)	KBr
518	X-1015 as received	Irtran

BUTYL LATEX

519	Enjay 80-21 extracted from treated fabric	KBr
520	Enjay 80-21 as received	Irtran

POLYACRYLATE

521	Rhoplex K-87 extracted from treated fabric	KBr
522	Rhoplex K-87 as received	Irtran

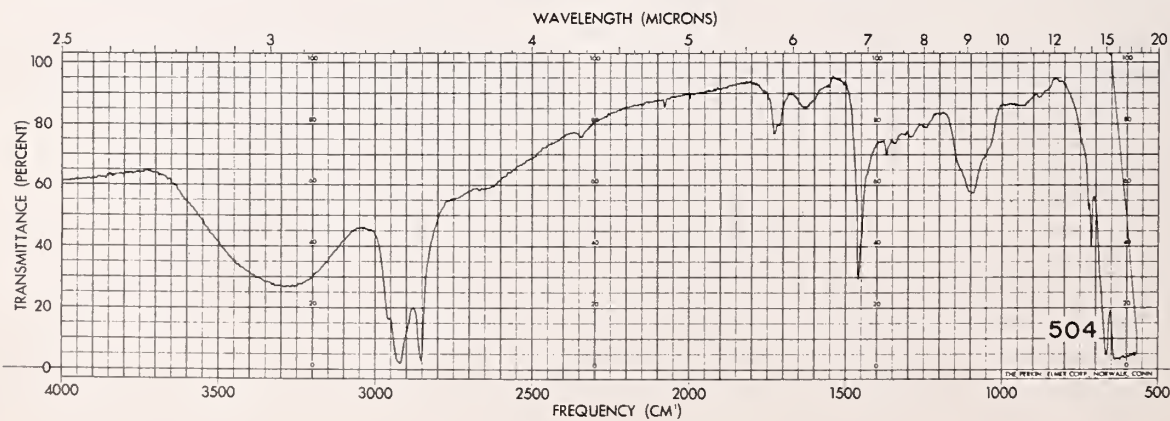
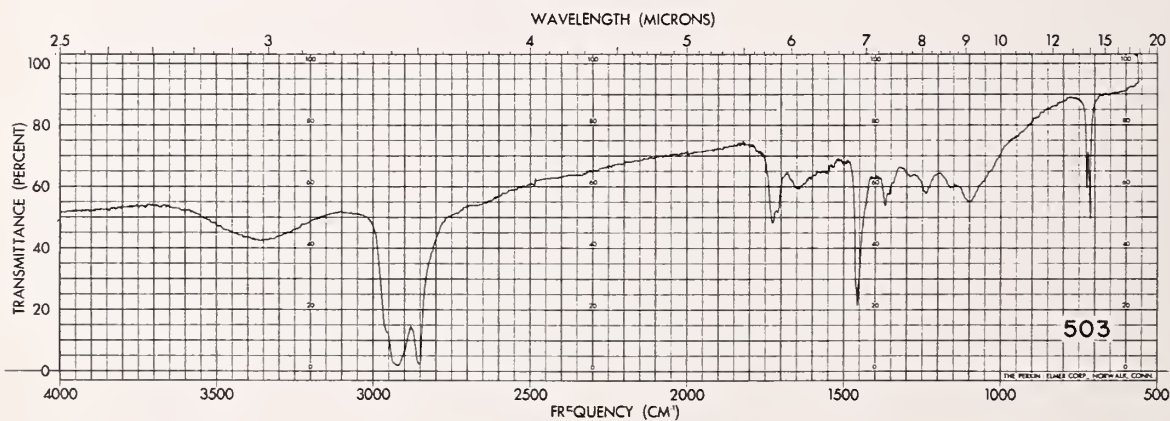
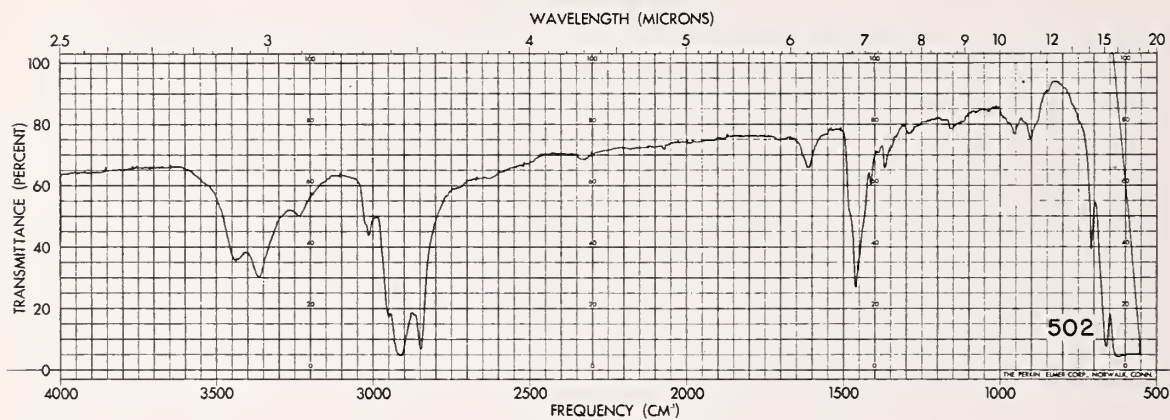
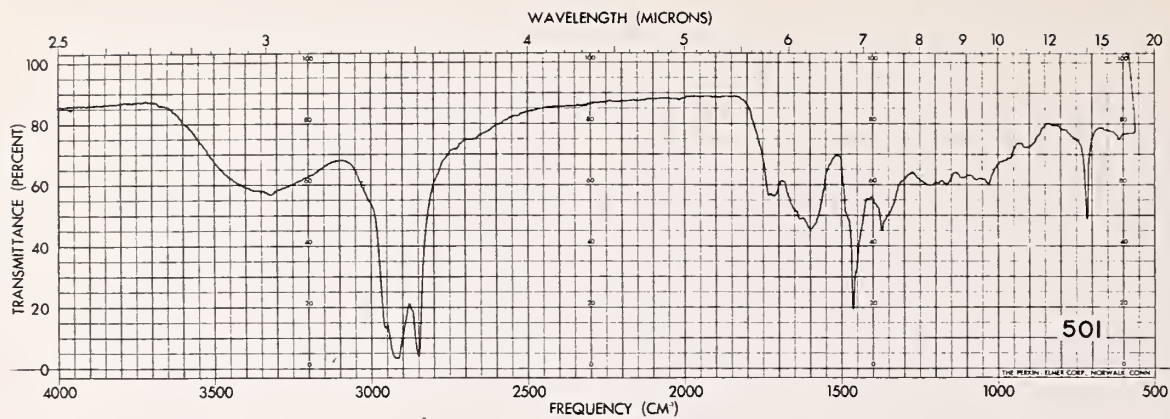
POLYOXYETHYLENE

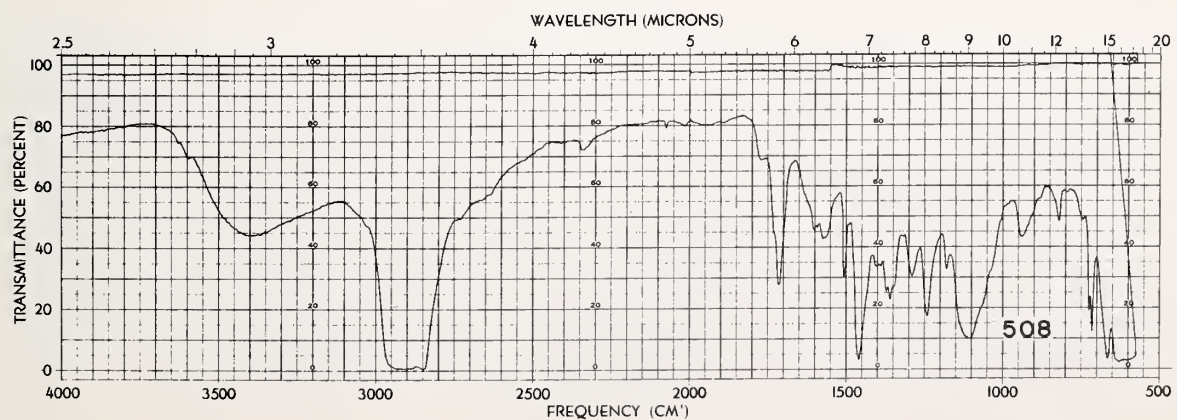
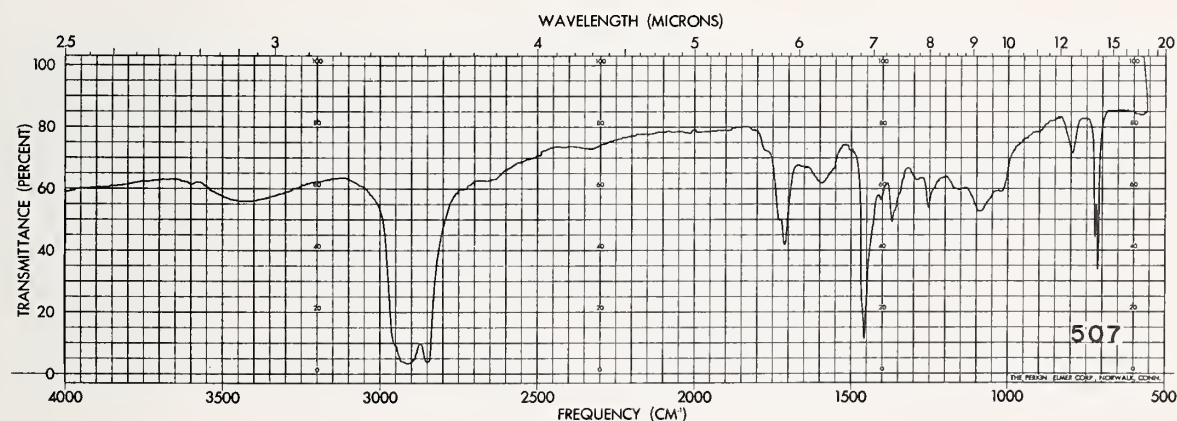
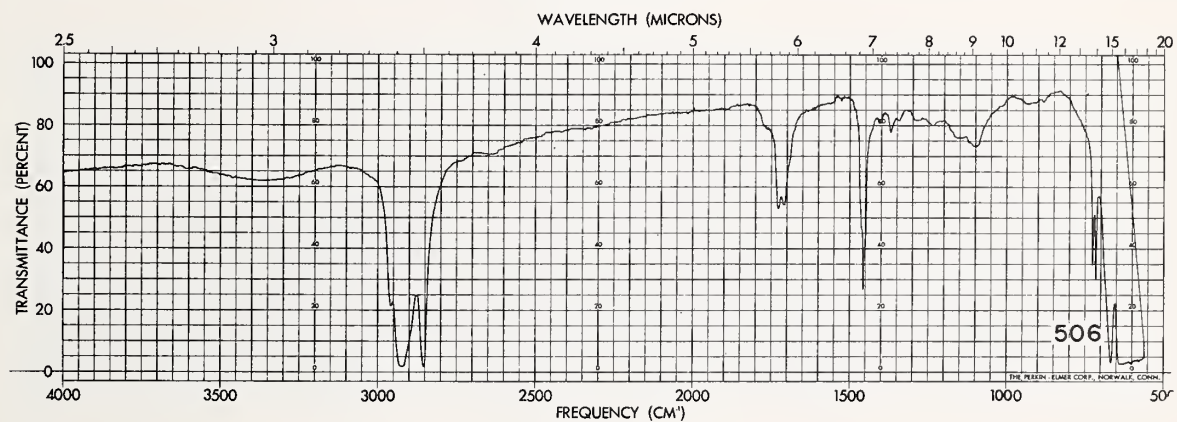
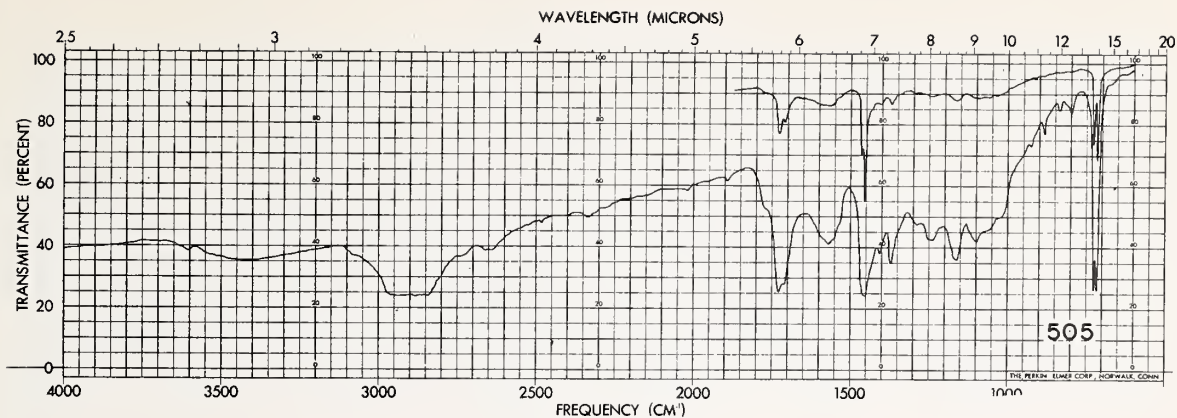
SORBITAN MONOPALMITATE

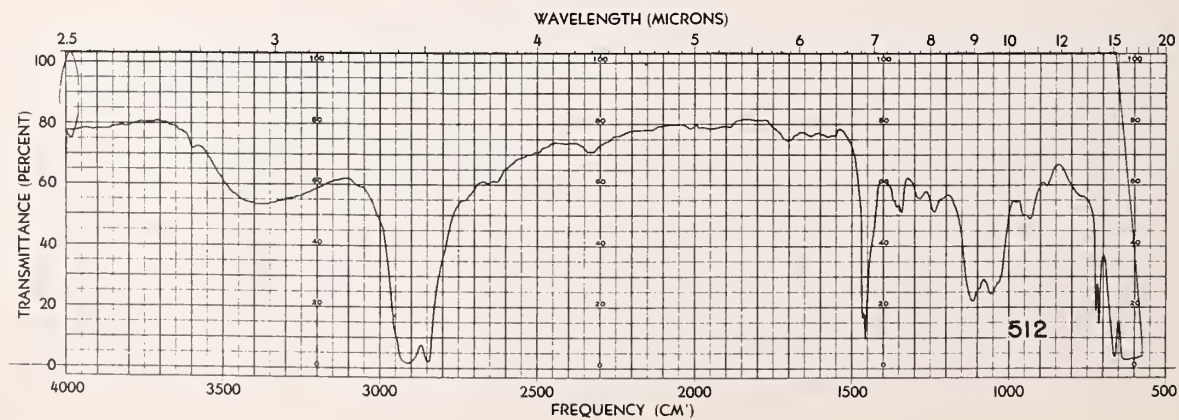
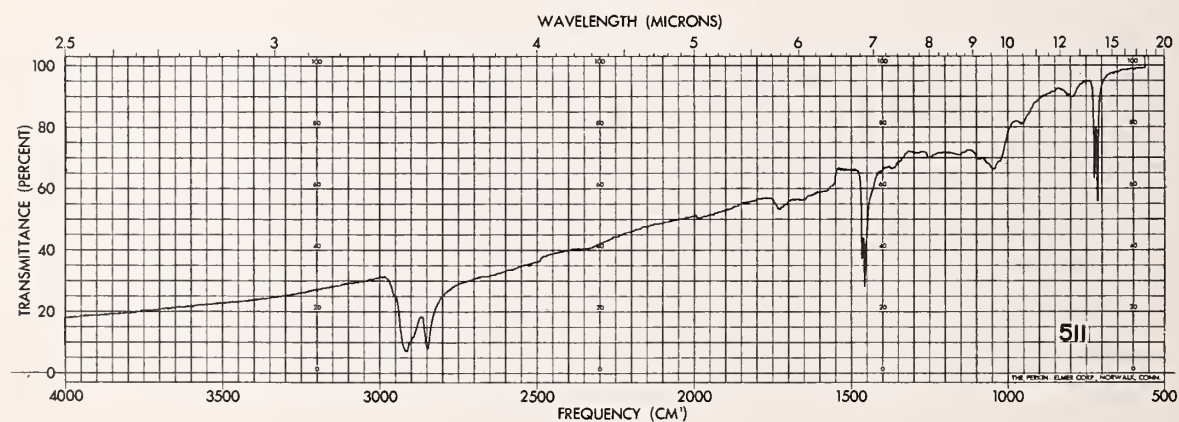
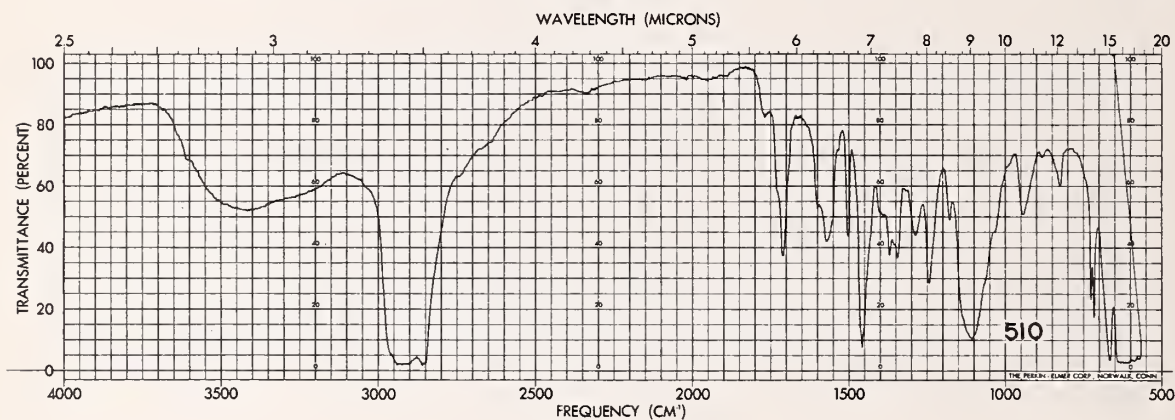
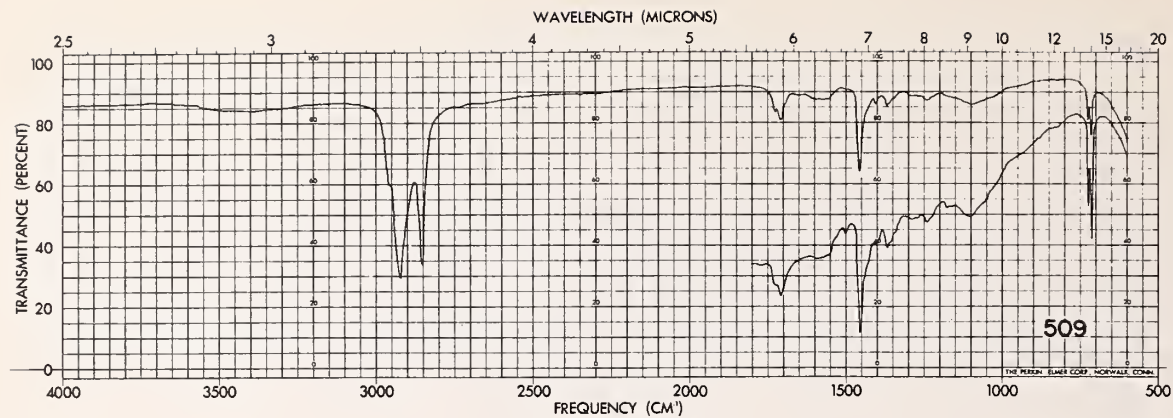
523	Tween 40 emulsifier extracted from treated fabric	KBr
524	Tween 40 emulsifier as received	Irtran

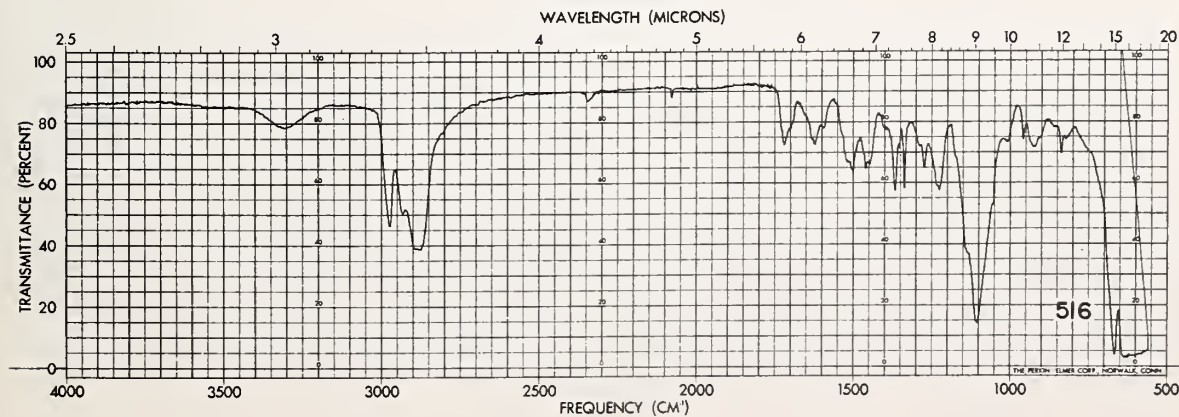
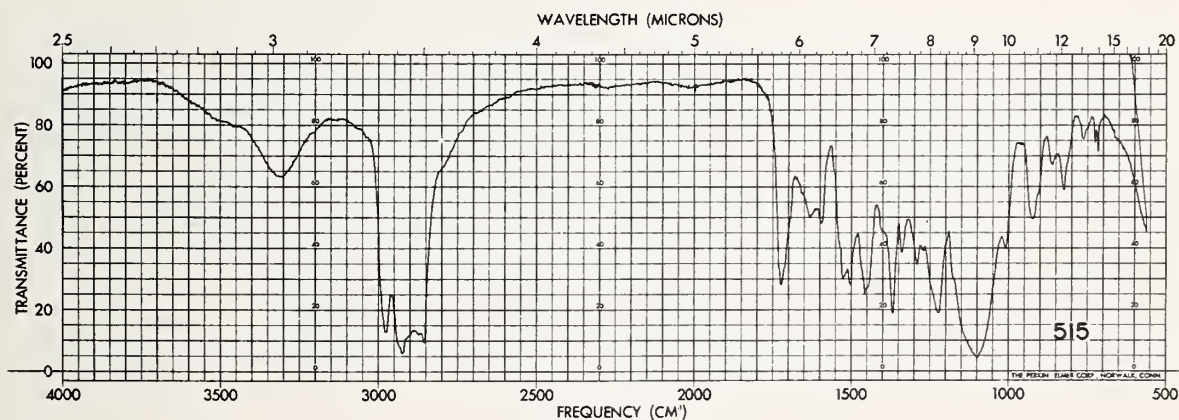
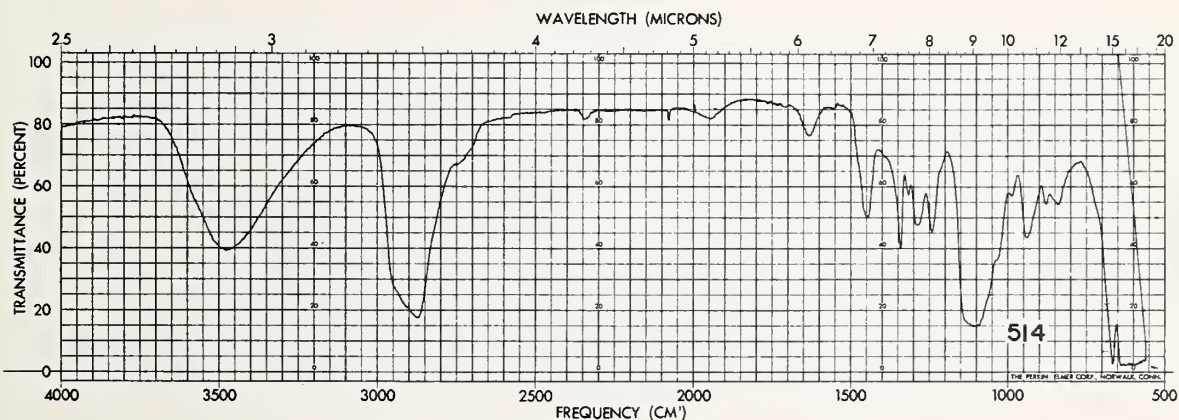
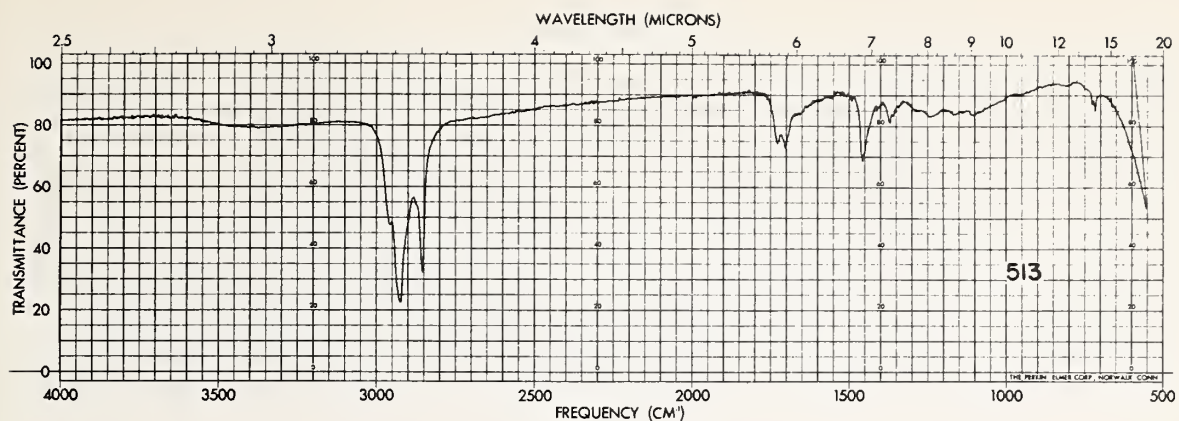
POLYSILOXANE

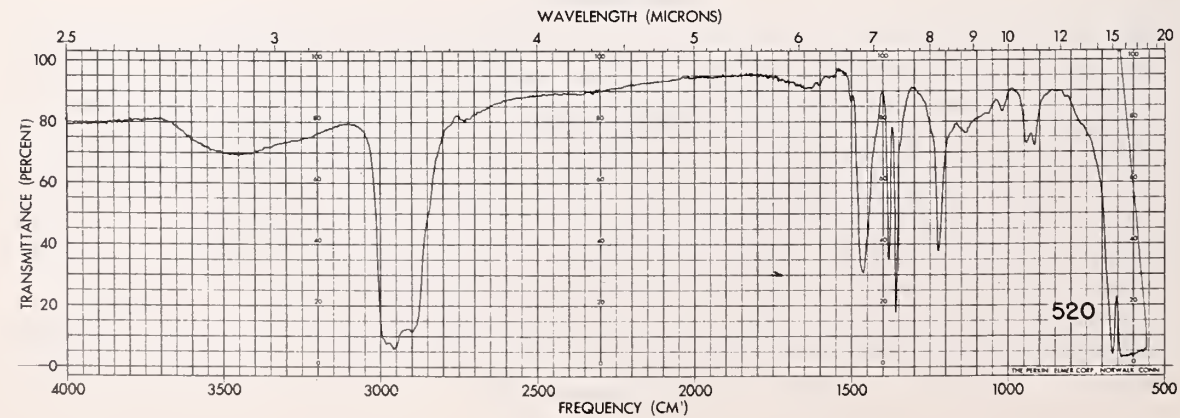
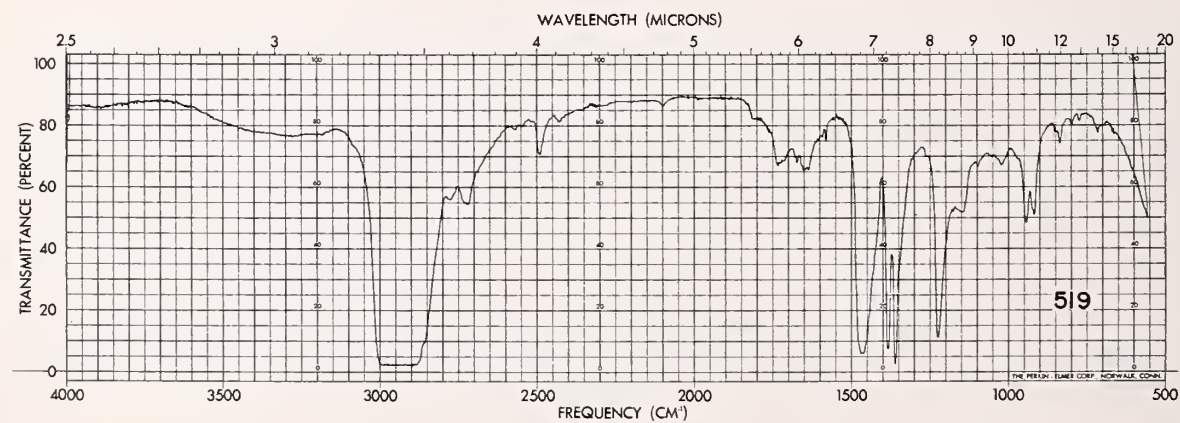
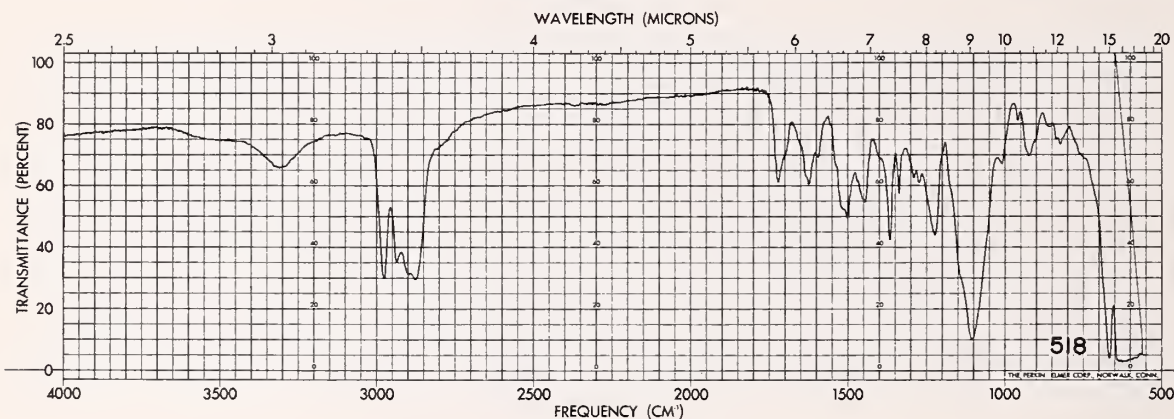
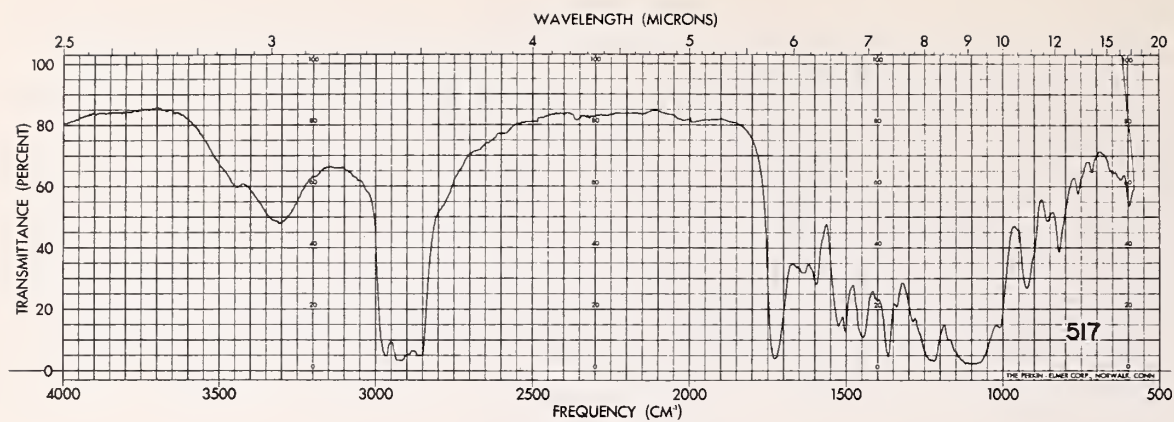
525	Syl-off DC-22 extracted from treated fabric	KBr
526	Syl-off DC-22 as received	Irtran

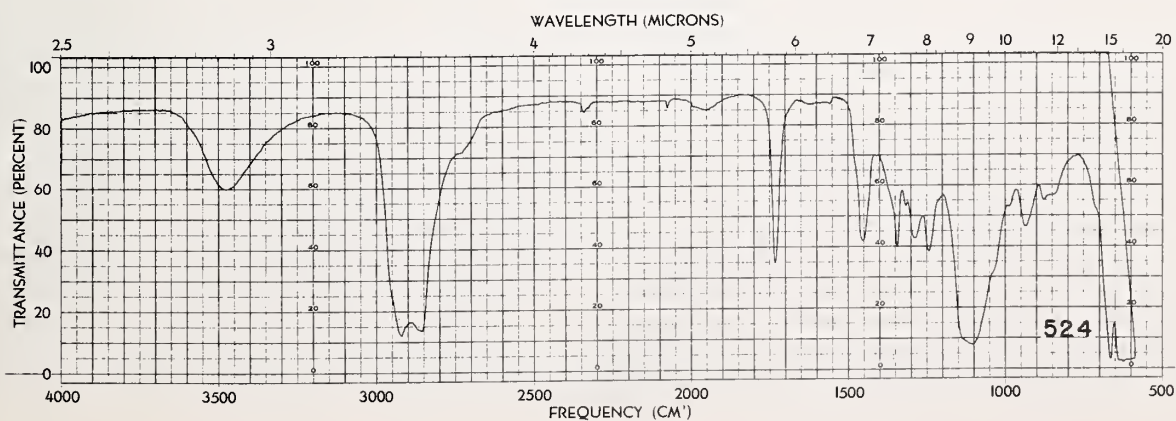
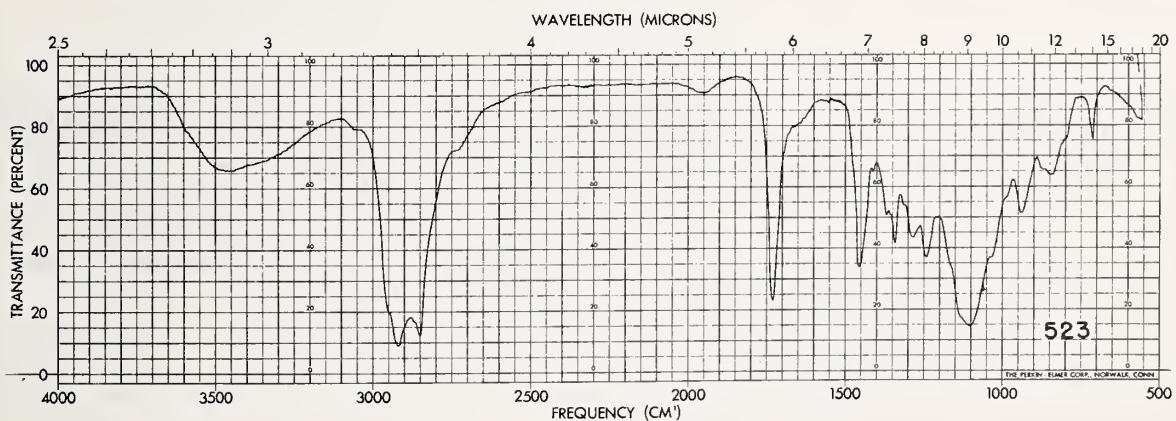
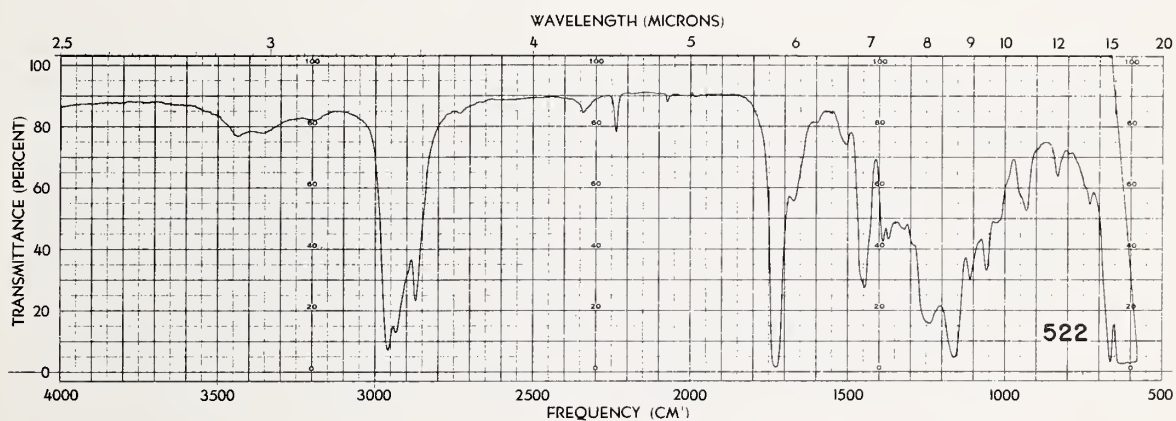
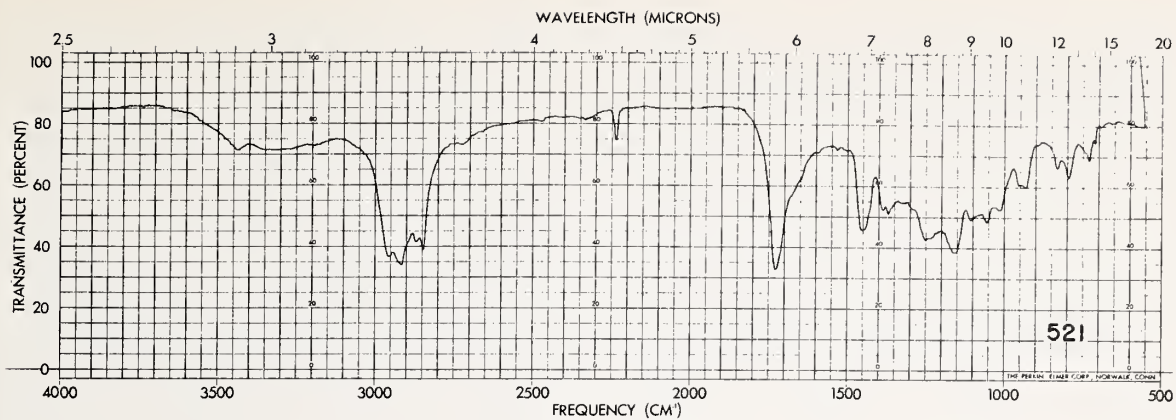


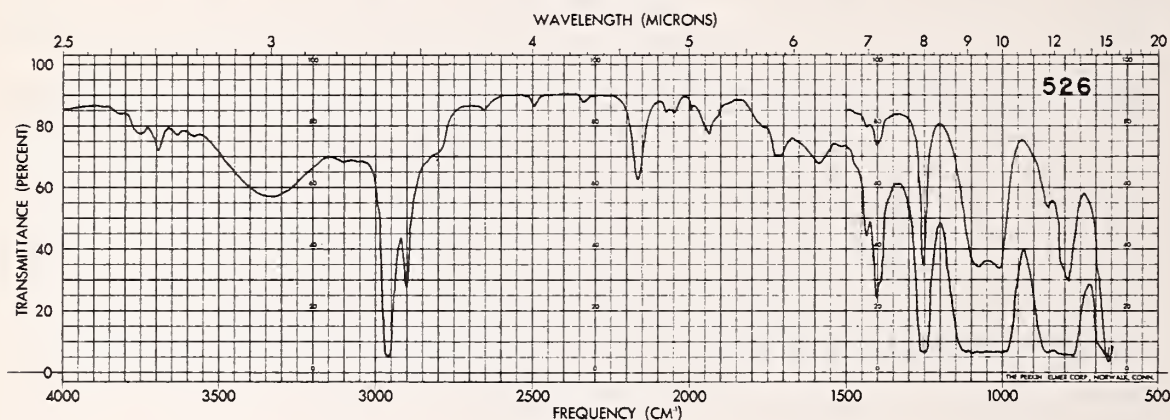
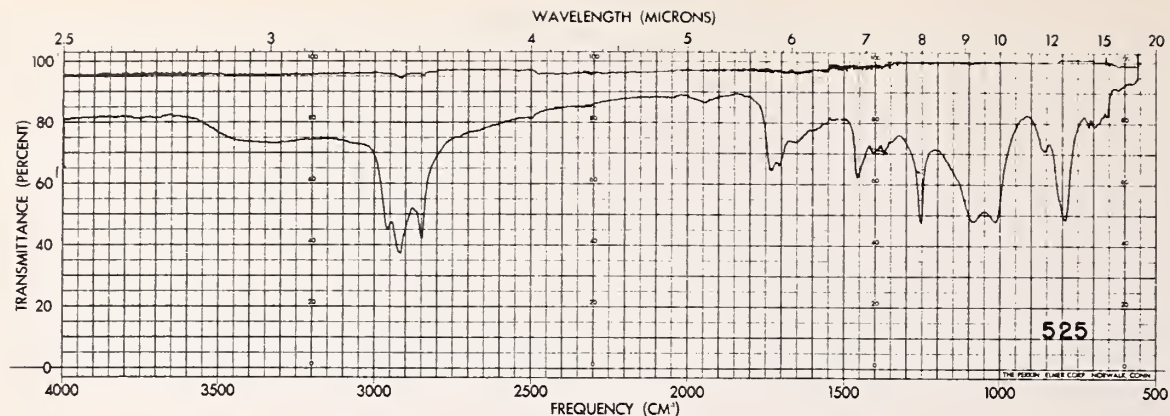












INFRARED ABSORPTION SPECTRA OF CHEMICAL FINISHING AGENTS HYDROLYZED BY 0.1 N HYDROCHLORIC ACID

Nineteen chemical finishing agents were removed in the solvent separation-extraction scheme with hydrochloric acid. The fabrics were hydrolyzed by the method of Miles et al. (8) as follows: Approximately 0.2 g of thoroughly dried fabric, cut into small pieces, was refluxed for 5 ± 0.5 minutes on a preheated hotplate with 5 ml of 0.1 N HCl. The solution was immediately decanted into a 50-ml round-bottom flask containing 2 ml of distilled water and 350 mg of spectral grade KBr, which was immersed in an ice-salt bath. The resulting mixture was kept cold to prevent further hydrolysis until it was evaporated to dryness under vacuum in a rotary evaporator at 28° C. The residue was further dried over P_2O_5 in vacuo for 16 hours. Approximately 50 mg of the dried residue was mixed with 300 mg of spectral grade KBr, and 300 mg of this mixture was formed into a half-inch disk

in a laboratory press and die. The quantity of residue was varied in order to give spectra of the desired intensity.

These acid hydrolyzates are nitrogenous cross-linking agents applied to the fabric to impart durable-press, wash-wear, or permanent-crease properties. The acid hydrolysis is a late step in the solvent separation-extraction procedure and presumably most of the chemical finishing agents that may have accompanied the treatment with the nitrogenous cross-linking agents will have been removed during previous steps. In the preparation of these spectra the samples were treated with trichloroethylene to remove the softeners, sizes, emulsifiers, etc. soluble in this solvent. The spectra (001-058) are presented in sets of three: (1) a spectrum of the fabric containing the chemical finish, (2) the acid hydrolysis product from the fabric after treatment with

0.1 N HCl, and (3) the spectrum of the pure unmodified chemical reagent obtained from the bottle.

All spectra except 028, 040, and 046 were obtained from KBr disks prepared according to the method described by O'Connor et al. (9). Spectra of MMM (028), DMHEC (040), and DMIBC (046) were prepared by smearing a thin film of the aqueous solution of the resin onto an Irtran plate and allowing it to dry at room temperature. The methylol derivatives of several of the cross-linking reagents have not been isolated. Spectrum 022 was obtained by preparing a disk of the material from a mixture of ethyl triazone and formalin (37 percent). Spectra of unmethylolated compounds included in this catalog are TCEA (049), TCEP (052), and TCPO (055).

The spectra of the chemical agents removed with 0.1 N HCl are characterized particularly by two sets of absorption bands, one in the 1500–1640-cm⁻¹ region, the other in the 700–800-cm⁻¹ region. The first series of bands arise from vi-

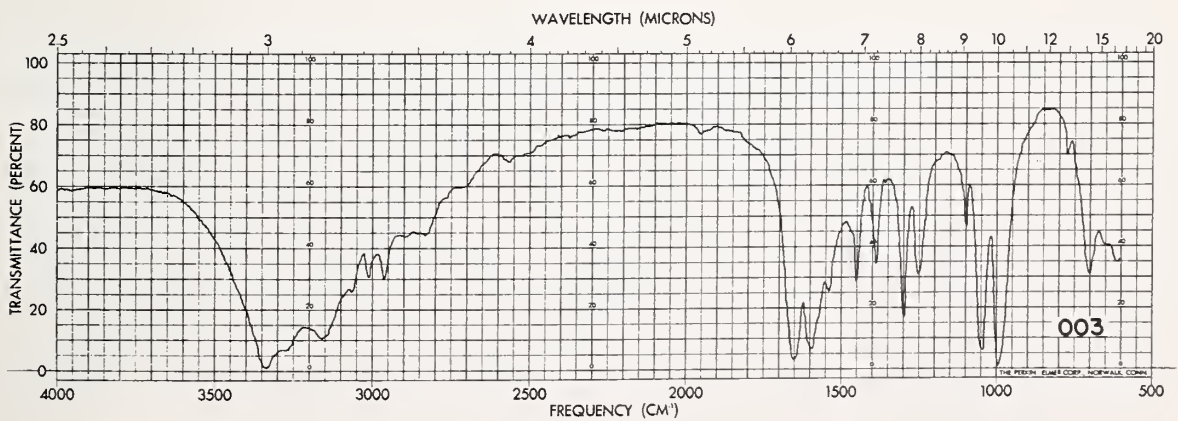
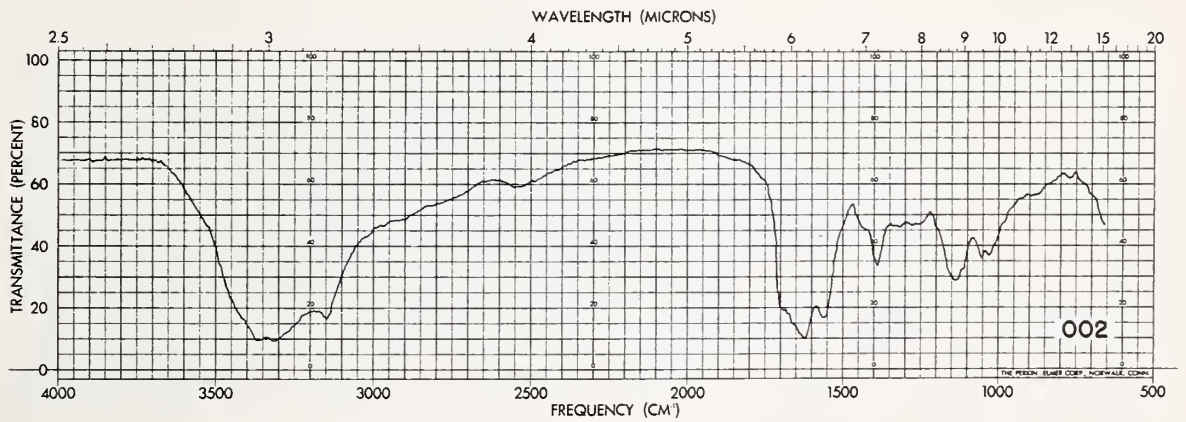
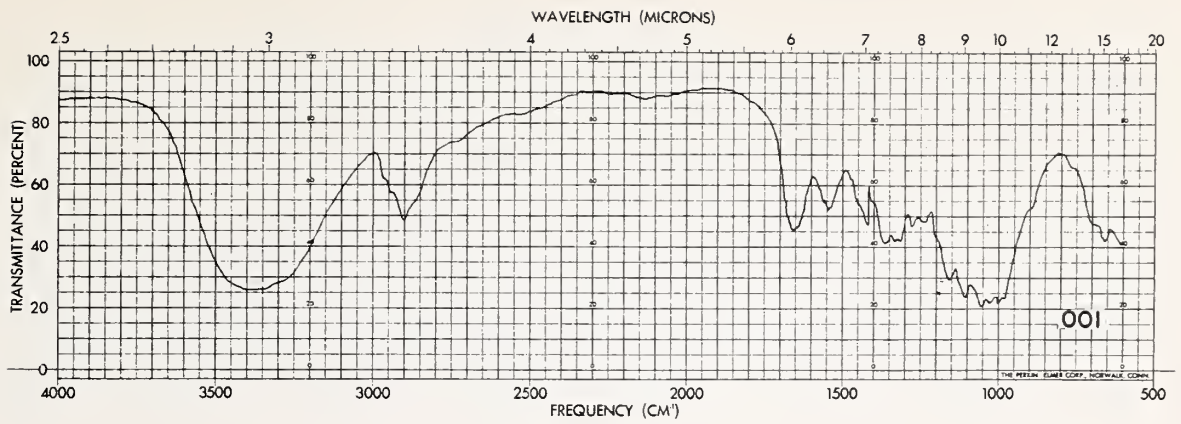
brations of the R—C(O)NH₂ group. Between 1600–1640 cm⁻¹ are the amide I bands arising from a stretching vibration of the C=O group in the amide. The amide II band accounts for the bands between 1500–1550 cm⁻¹ generally attributed to the C—N bands exhibiting C=N character or to a combination band of the N—H bending with the C=O stretching in the amide group (2). The exact frequencies of the maximum absorption vary with the molecular environment, and direct comparison of the unknown with the library of standard reference spectra will permit qualitative identification. The second series of bands, from 700–800 cm⁻¹, arise from various bendings of C—H groups about ring structures and are quite characteristic of the ring structure and the positions of the C—H groups on the rings. (Detailed analyses of these bands have been published; see references 6 and 8.)

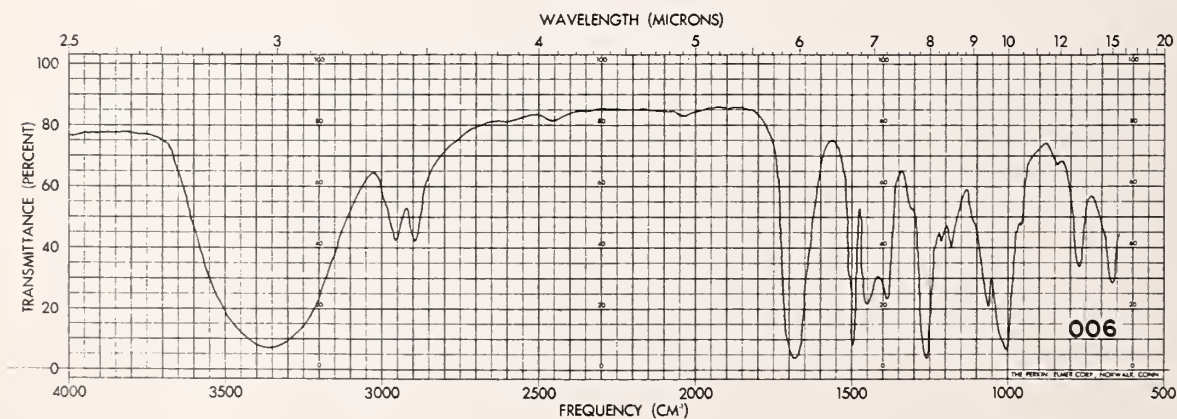
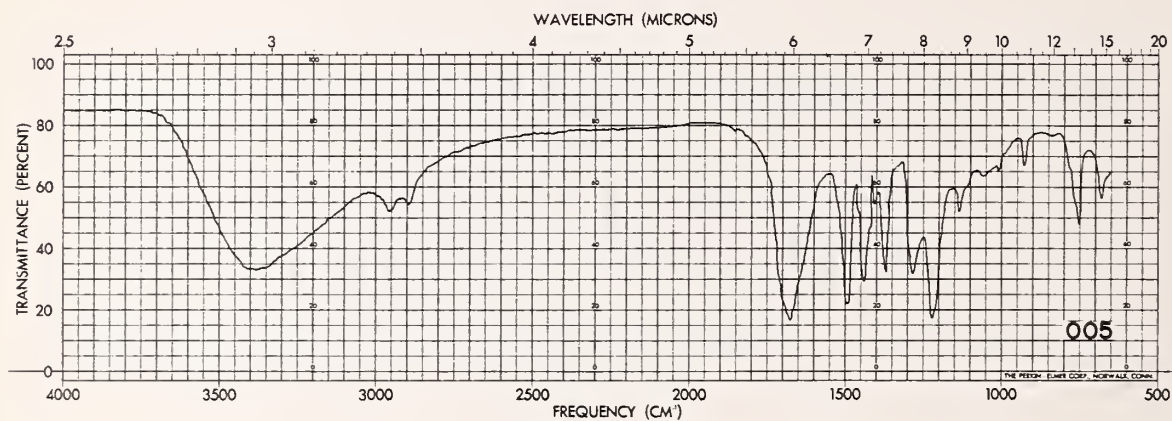
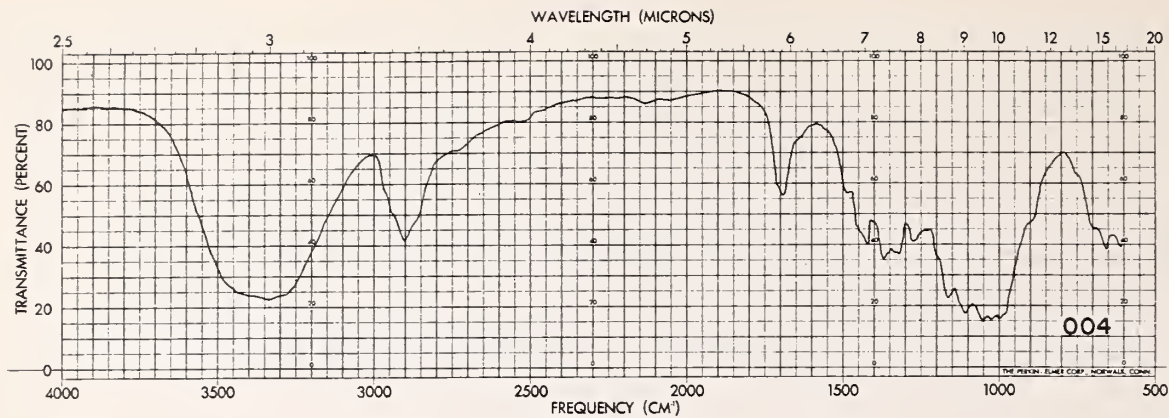
The finishing agents are listed below and referenced to the spectra which follow.

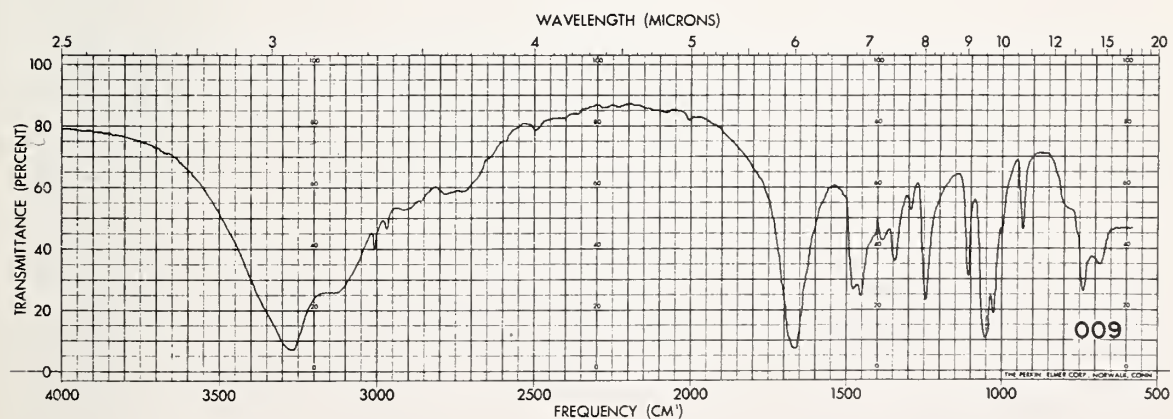
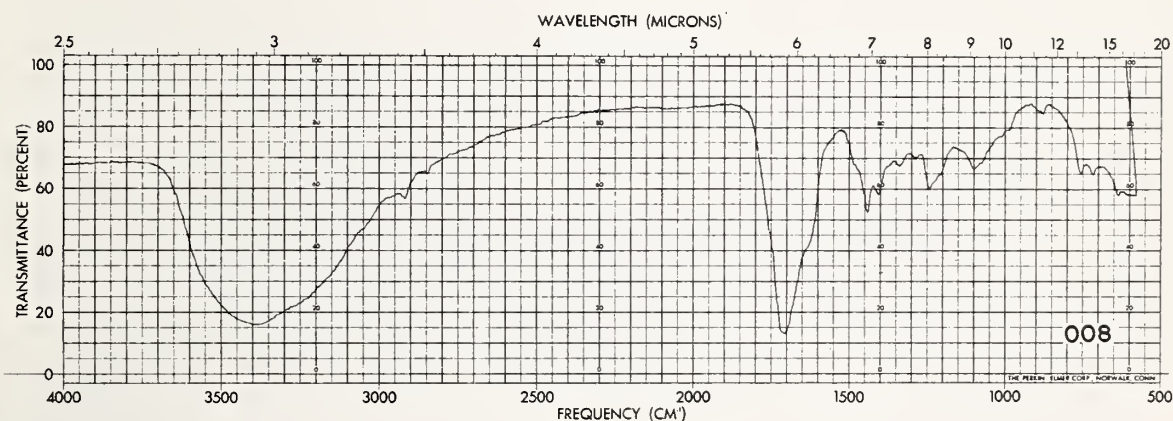
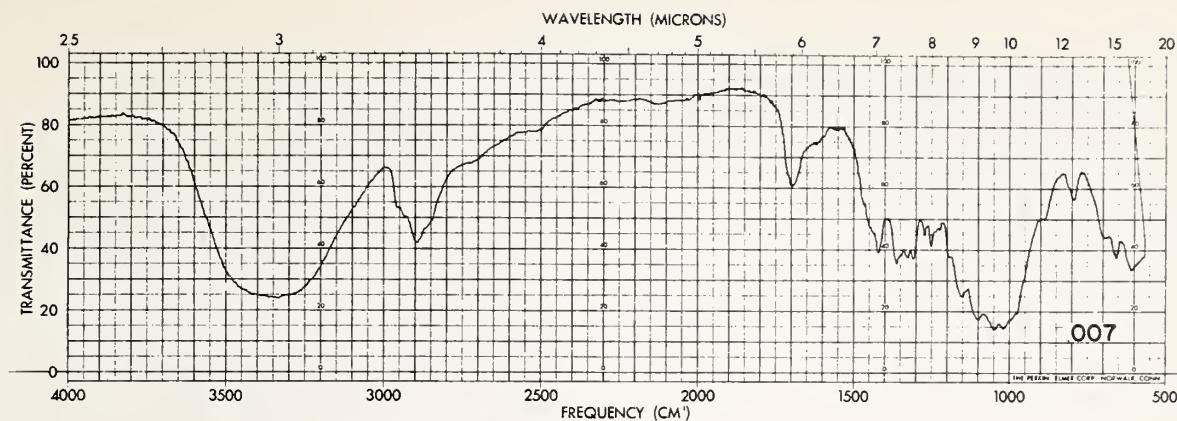
<i>Spectrum No.</i>	<i>Description</i>
001	Fabric treated with dimethylolurea (DMU).
002	Acid hydrolyzate of fabric treated with DMU.
003	DMU.
004	Fabric treated with dimethylolethyleneurea (DMEU).
005	Acid hydrolyzate of fabric treated with DMEU.
006	DMEU.
007	Fabric treated with dihydroxyethyleneurea (DHEU).
008	Acid hydrolyzate of fabric treated with DHEU.
009	DHEU.
010	Fabric treated with dimethyloldihydroxyethyleneurea (DMDHEU).
011	Acid hydrolyzate of fabric treated with DMDHEU (Fixapret CP40).
012	Acid hydrolyzate of fabric treated with DMDHEU (Permafresh 183).
013	DMDHEU.
014	Fabric treated with dimethylolpropyleneurea (DMPU).
015	Acid hydrolyzate of fabric treated with DMPU.
016	DMPU.
017	Fabric treated with dimethyloluron (DMUr).
018	Acid hydrolyzate of fabric treated with DMUr.
019	DMUr.
020	Fabric treated with dimethyloethyltriazone (DMET).
021	Acid hydrolyzate of fabric treated with DMET.
022	Ethyltriazone-formalin mixture.
023	Fabric treated with trimethylolmelamine (MM).
024	Acid hydrolyzate of fabric treated with MM.
025	MM.
026	Fabric treated with methylated trimethylolmelamine (MMM).
027	Acid hydrolyzate of fabric treated with MMM.

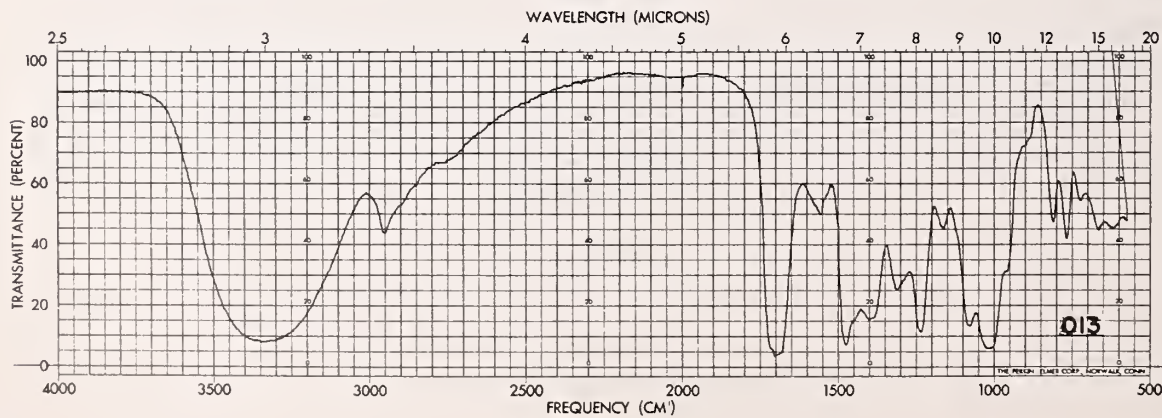
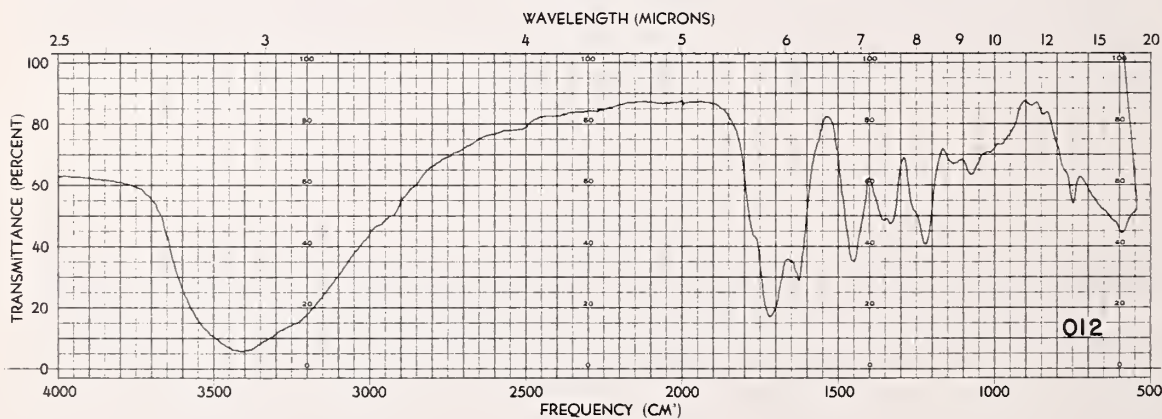
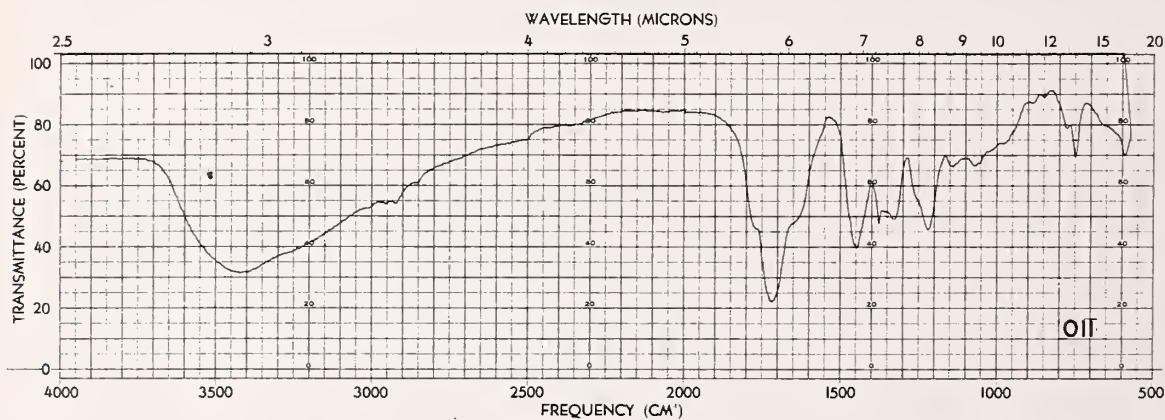
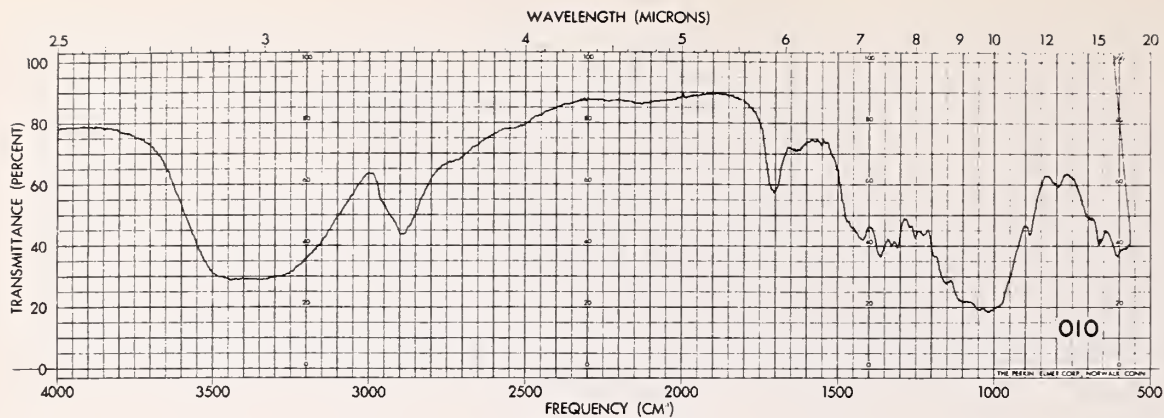
*Spectrum**No.**Description*

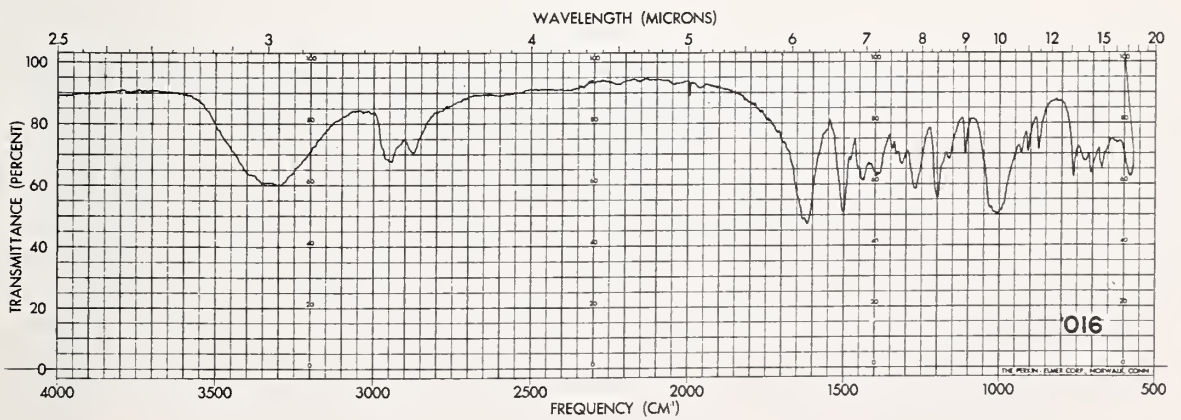
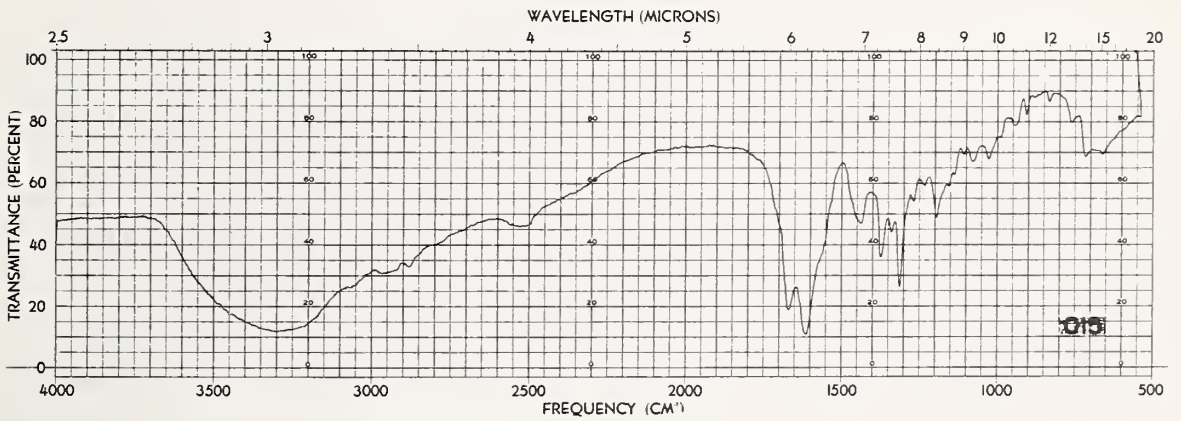
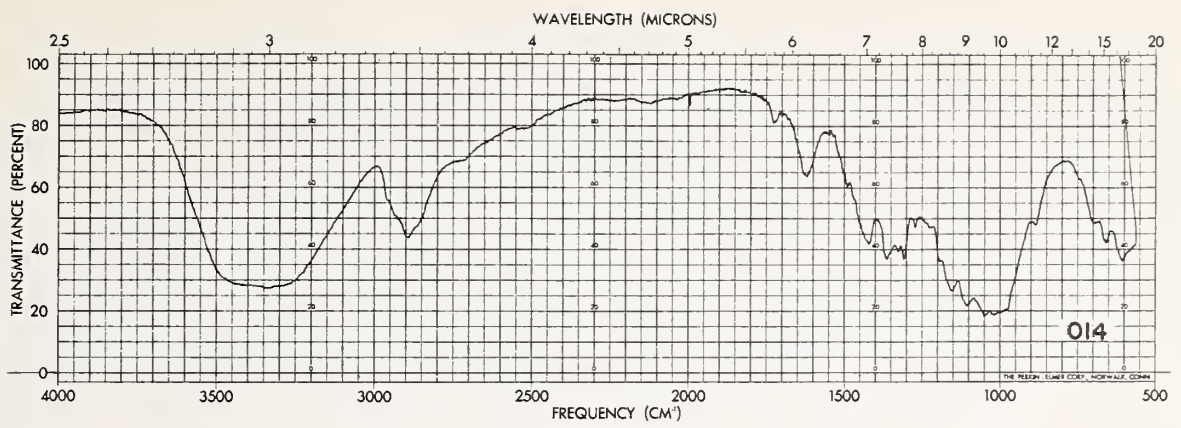
- | | |
|-----|--|
| 028 | MMM. |
| 029 | Fabric treated with <i>N</i> -methylolmethylcarbamate (MMMC). |
| 030 | Acid hydrolyzate of fabric treated with MMMC. |
| 031 | MMMC. |
| 032 | Fabric treated with dimethylolmethylcarbamate (DMMC). |
| 033 | Acid hydrolyzate of fabric treated with DMMC. |
| 034 | DMMC. |
| 035 | Fabric treated with dimethylolethylcarbamate (DMEC). |
| 036 | Acid hydrolyzate of fabric treated with DMEC. |
| 037 | DMEC. |
| 038 | Fabric treated with dimethylolhydroxyethylcarbamate (DMHEC). |
| 039 | Acid hydrolyzate of fabric treated with DMHEC. |
| 040 | DMHEC. |
| 041 | Fabric treated with dimethylolisopropylcarbamate (DMIC). |
| 042 | Acid hydrolyzate of fabric treated with DMIC. |
| 043 | DMIC. |
| 044 | Fabric treated with dimethylolisobutylcarbamate (DMIBC). |
| 045 | Acid hydrolyzate of fabric treated with DMIBC. |
| 046 | DMIBC. |
| 047 | Fabric treated with tris(methylolcarbamoylethyl) amine (TMCEA). |
| 048 | Acid hydrolyzate of fabric treated with TMCEA. |
| 049 | Tris(carbamoylethyl) amine (TCEA). |
| 050 | Fabric treated with tris(methylolcarbamoylethyl) phosphine
(TMCEP). |
| 051 | Acid hydrolyzate of fabric treated with TMCEP. |
| 052 | Tris(carbamoylethyl) phosphine (TCEP). |
| 053 | Fabric treated with tris(methylolcarbamoylethyl) phosphine oxide
(TMCPO). |
| 054 | Acid hydrolyzate of fabric treated with TMCPO. |
| 055 | Tris(carbamoylethyl) phosphine oxide (TCPO). |
| 056 | Fabric treated with tris (1-aziridinyl) phosphine oxide (APO). |
| 057 | Acid hydrolyzate of fabric treated with APO. |
| 058 | APO. |

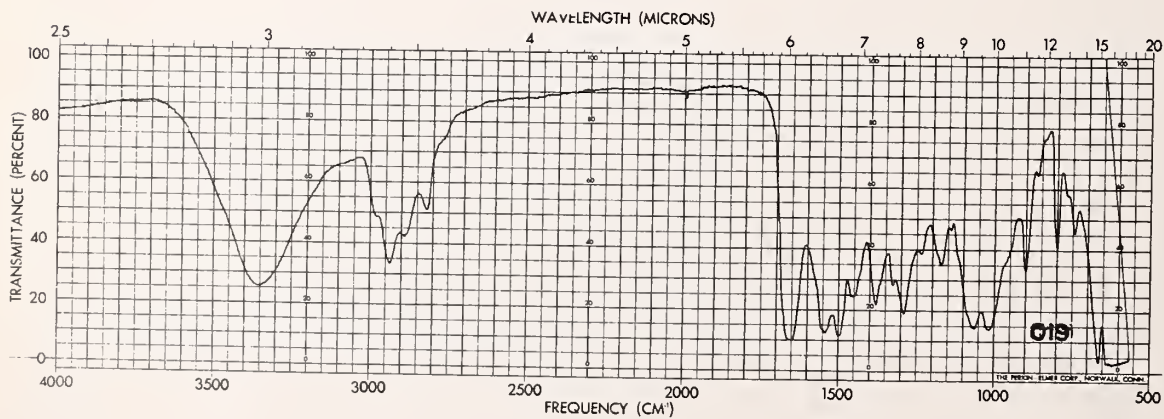
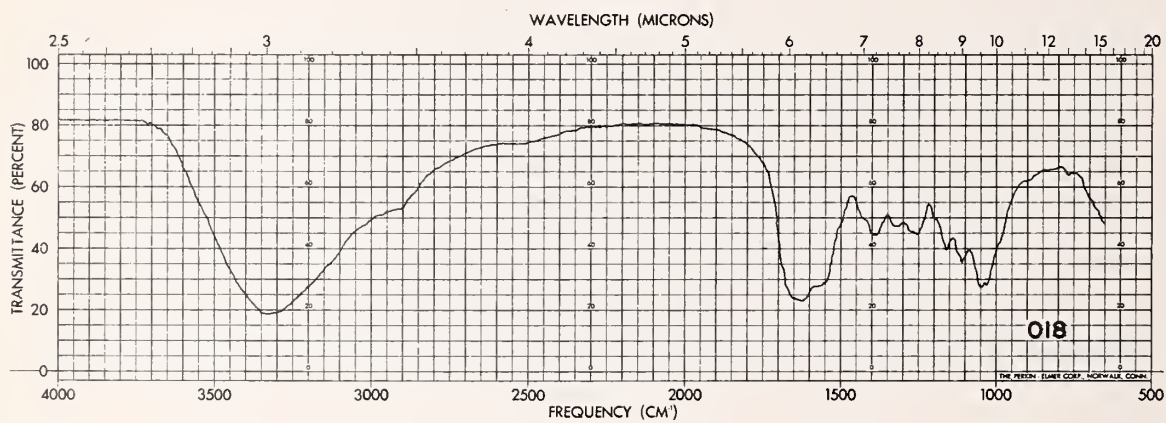
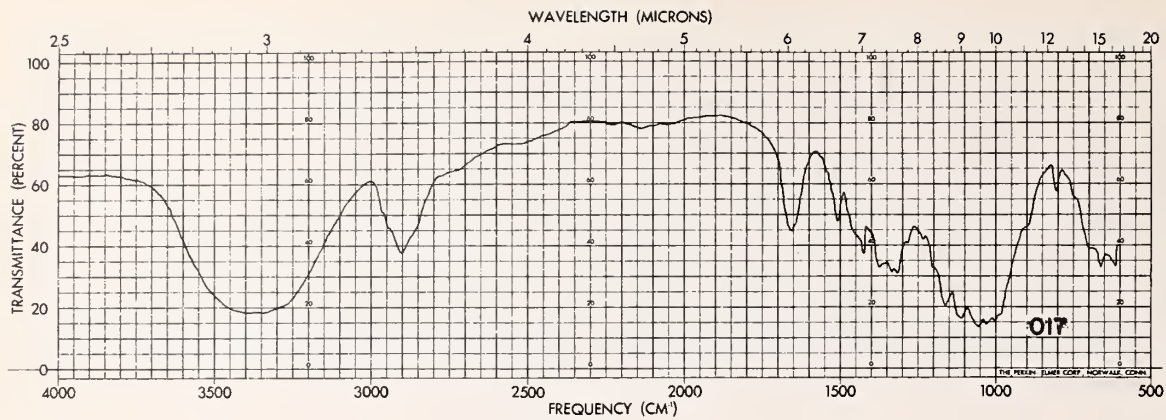


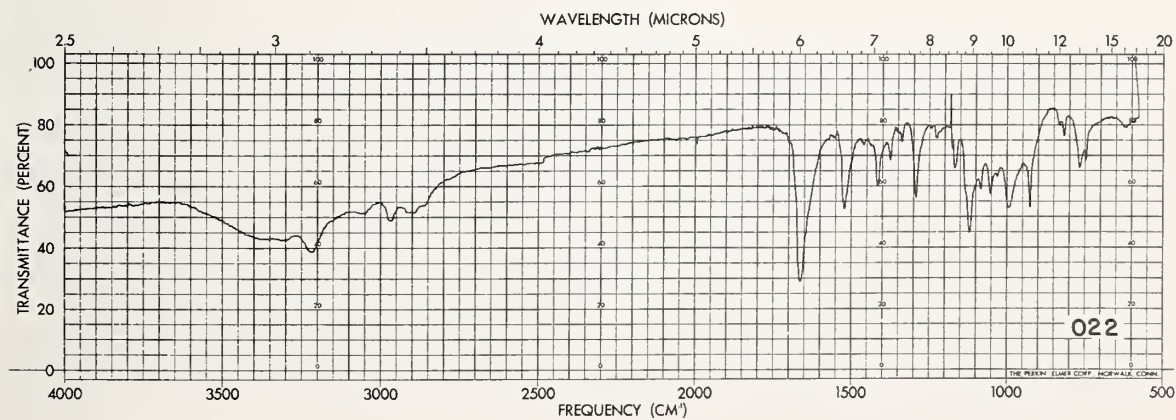
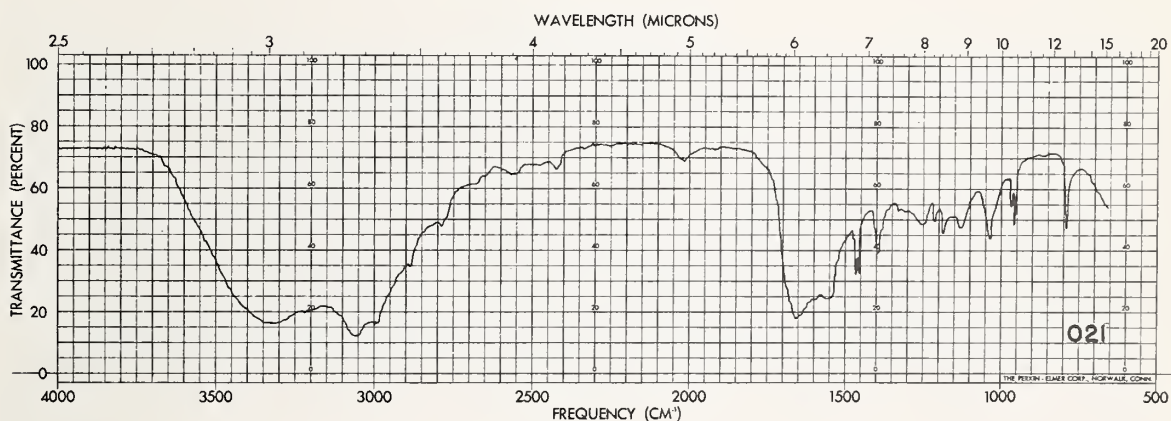
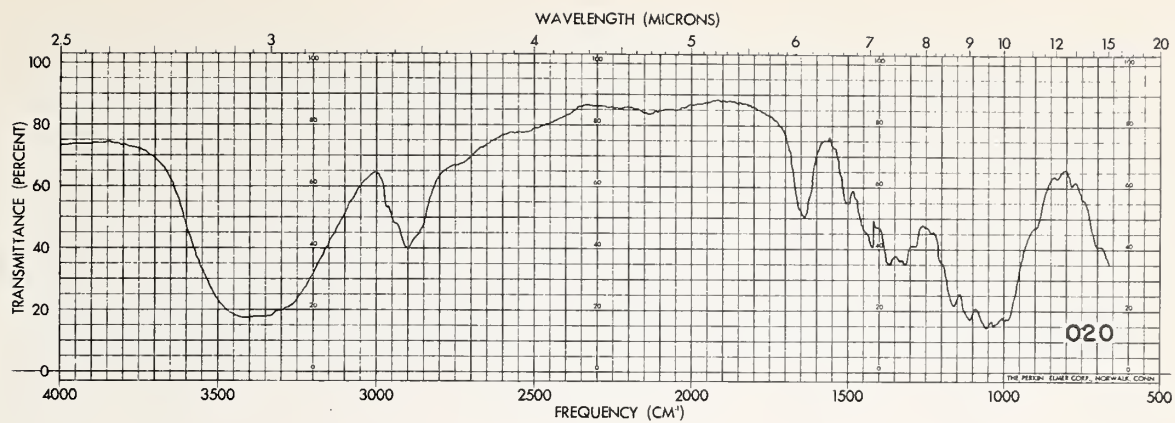




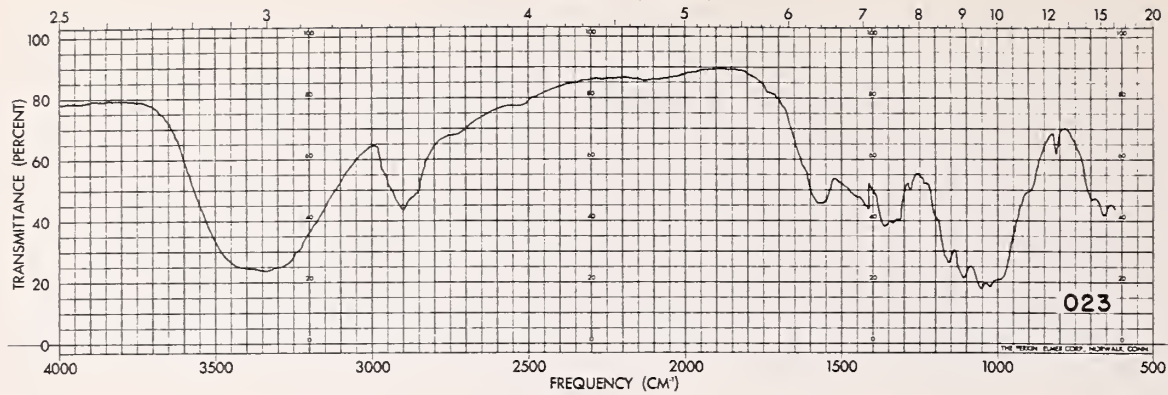




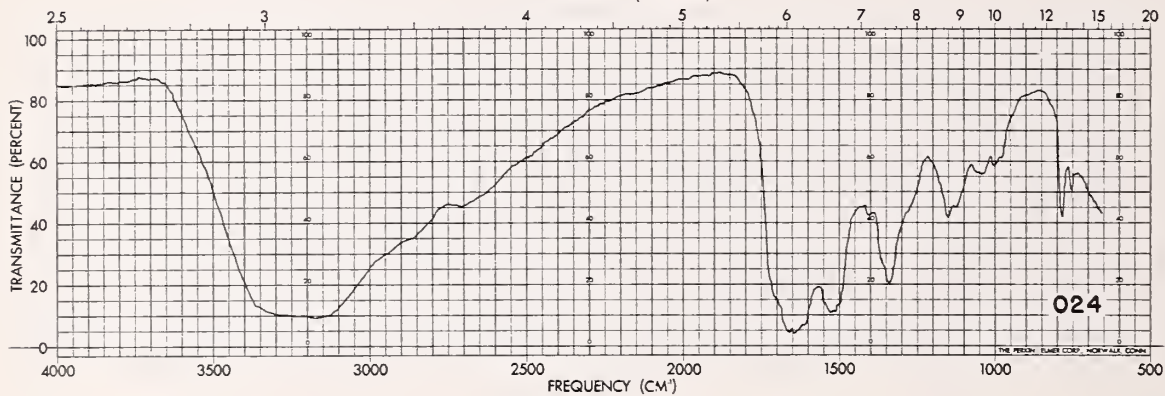




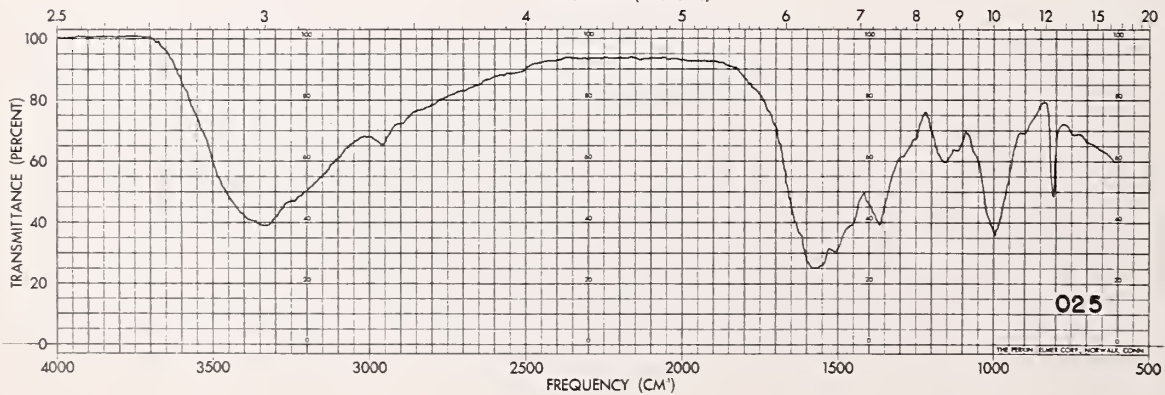
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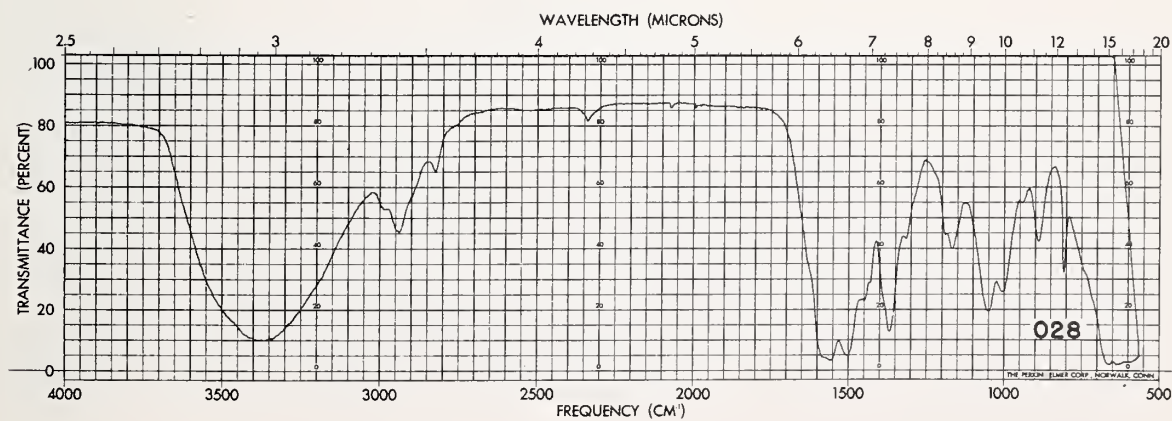
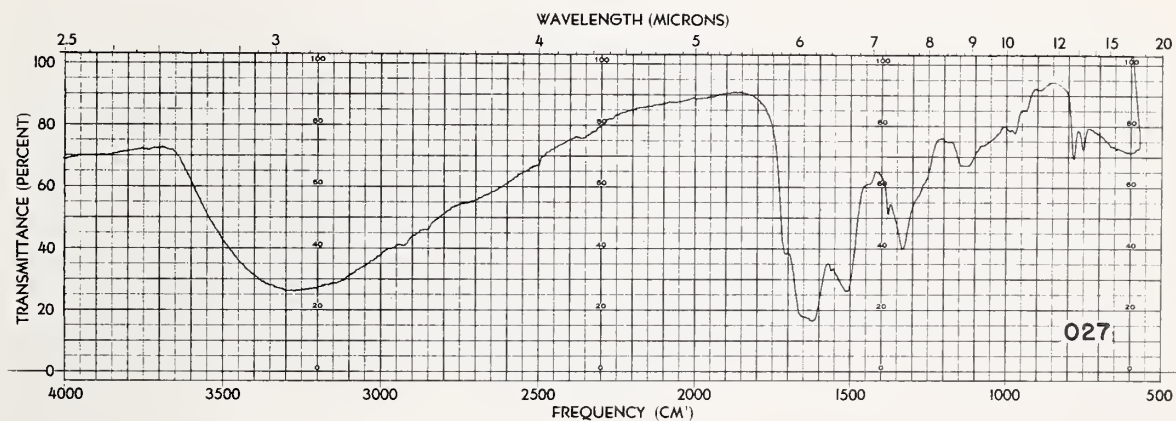
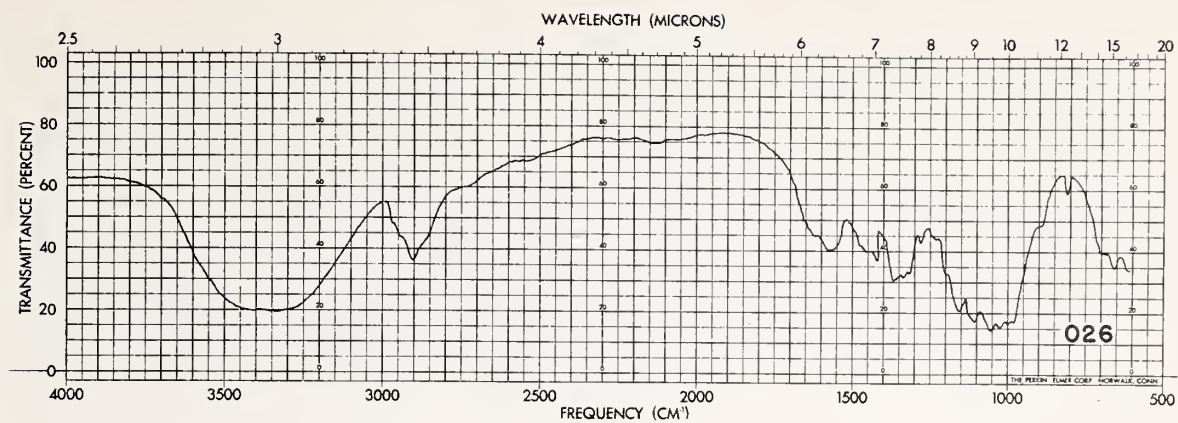


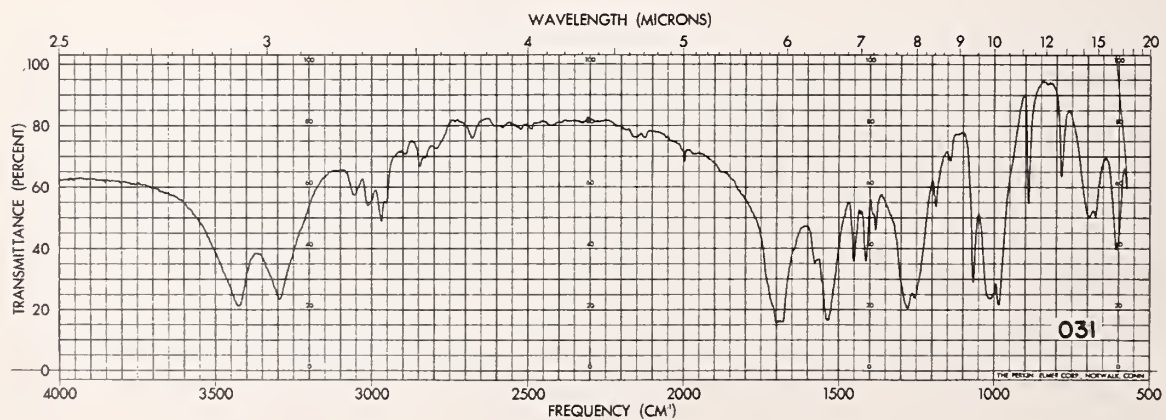
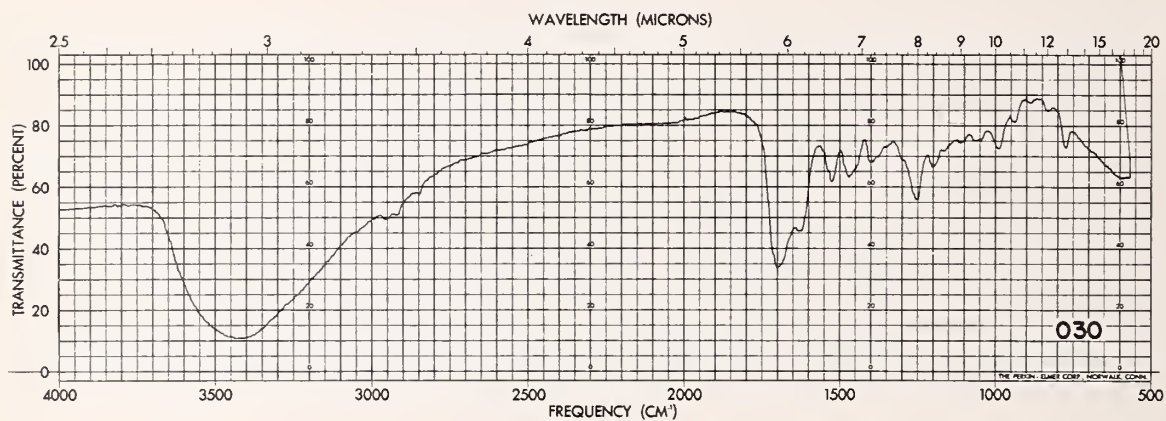
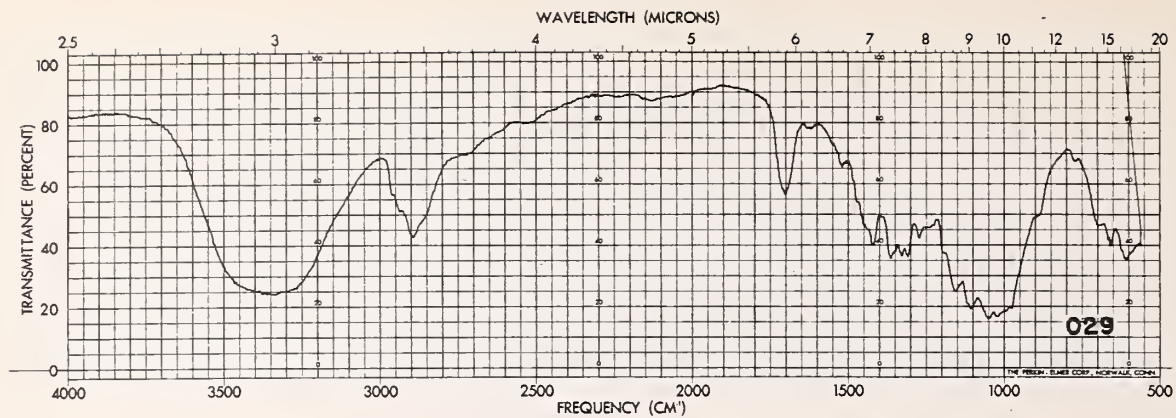
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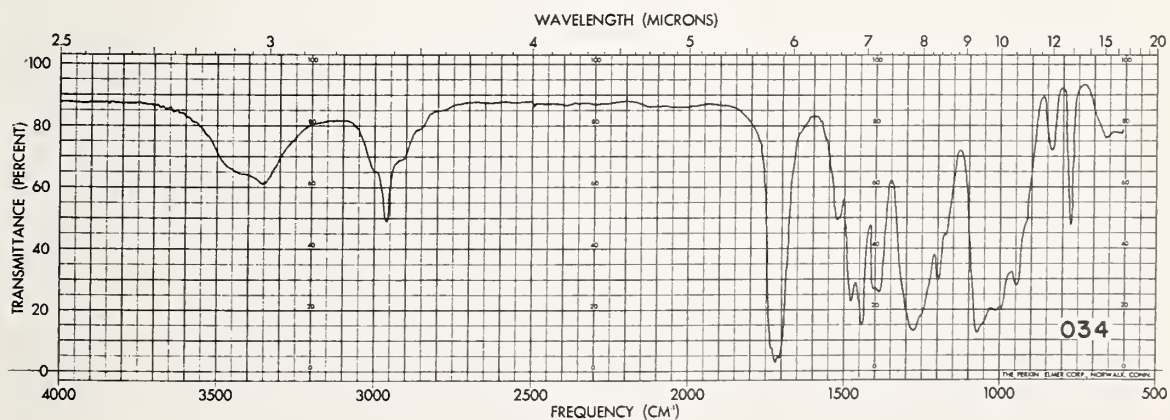
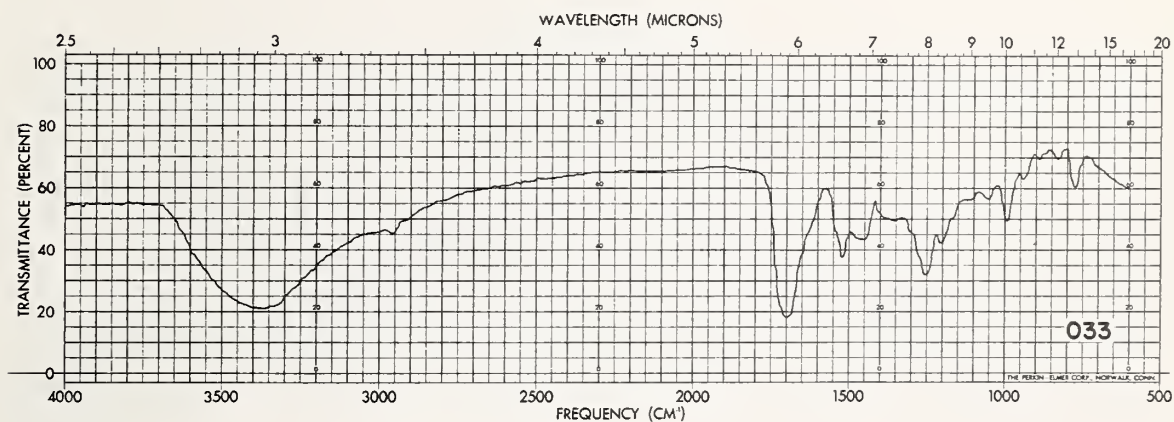
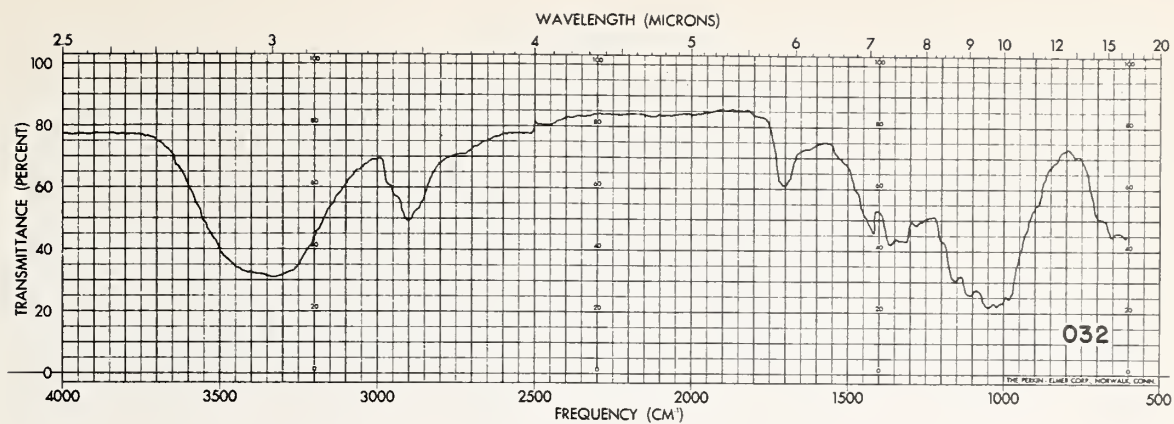


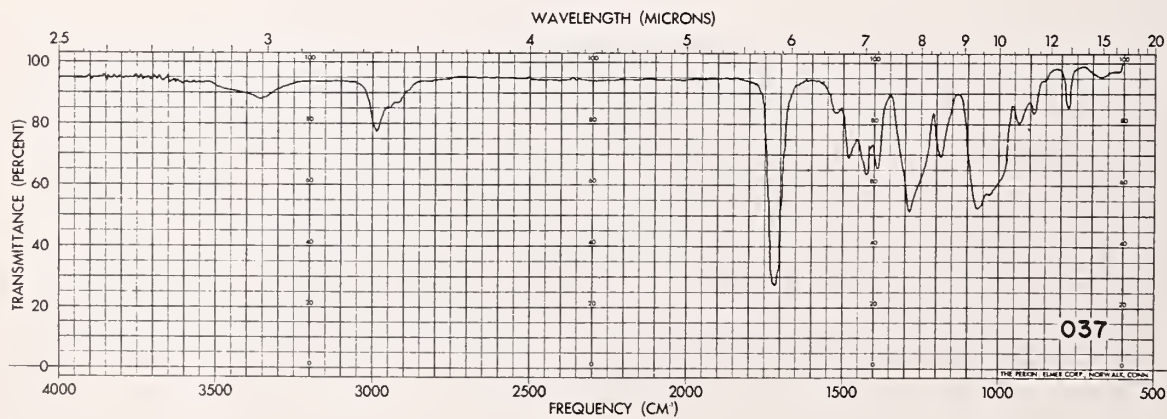
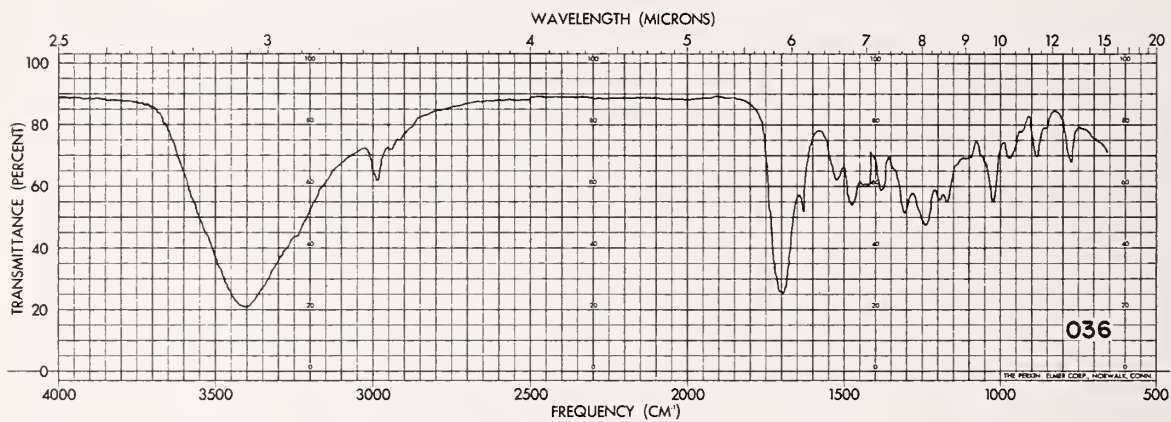
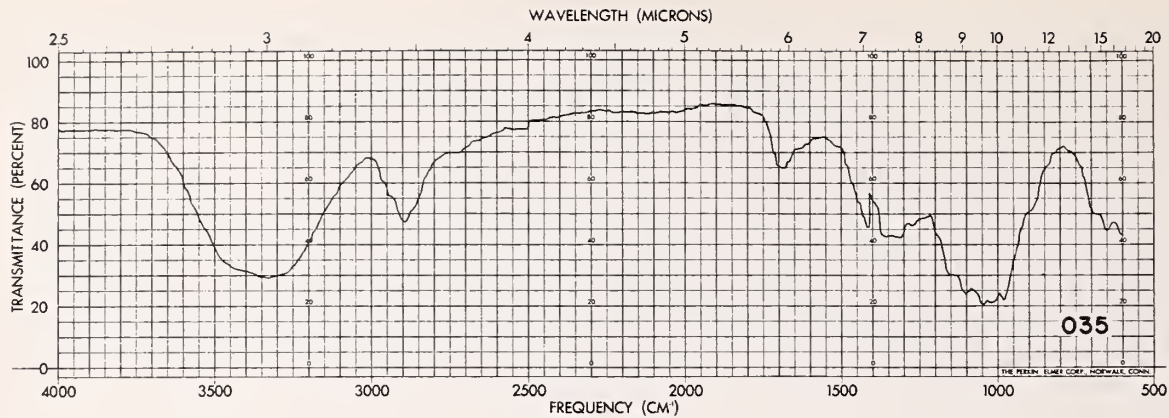
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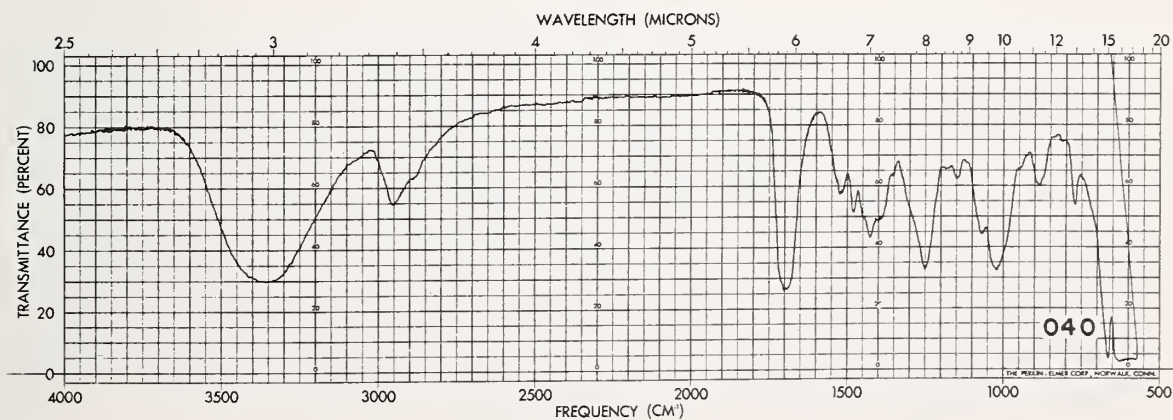
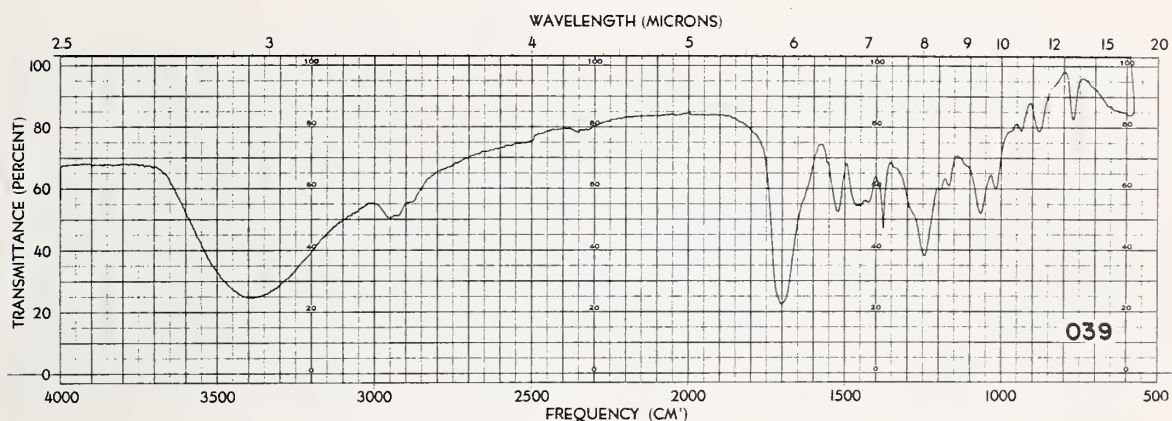
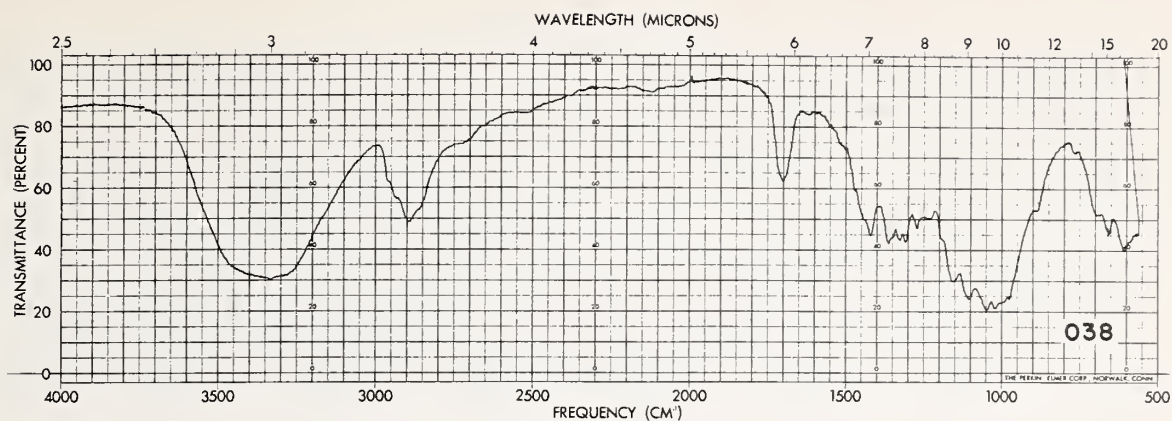


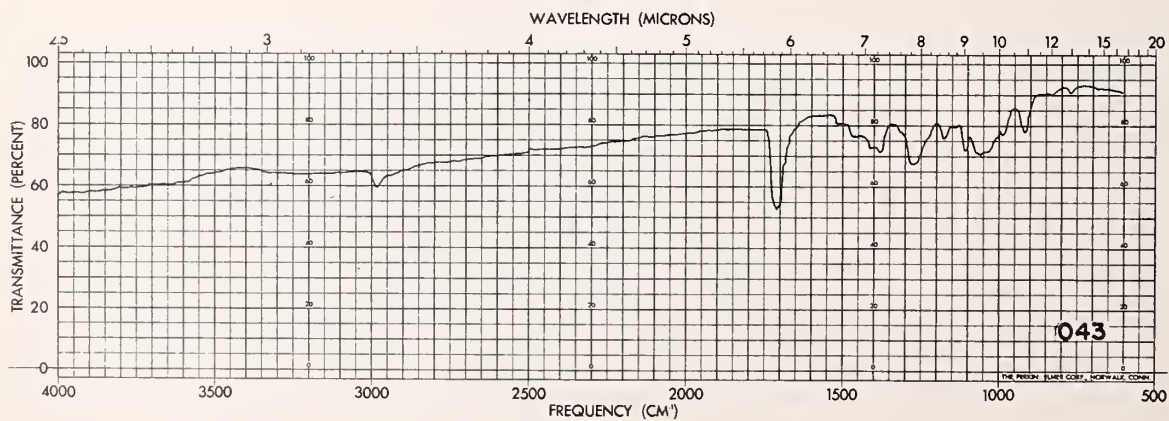
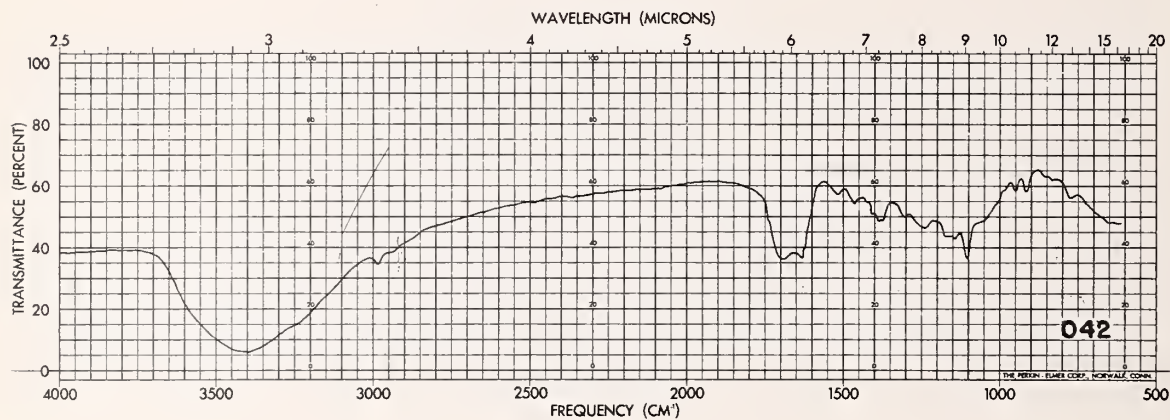
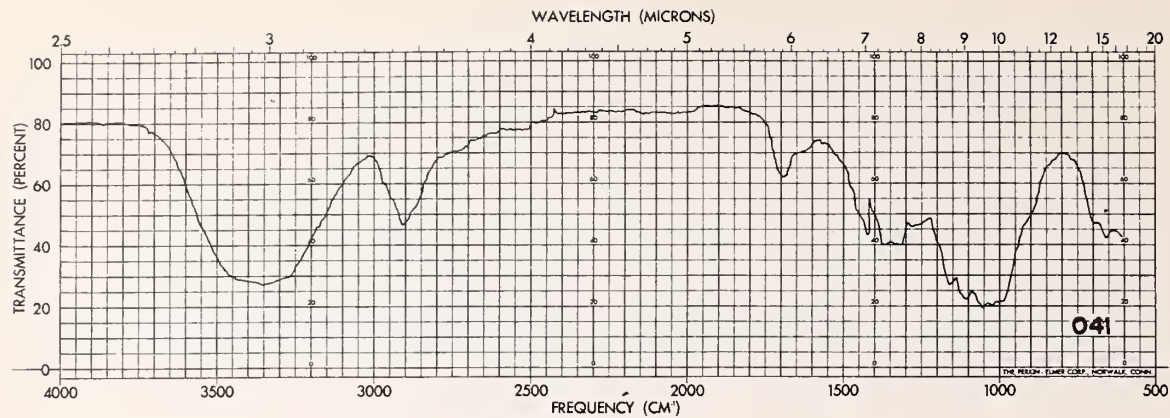


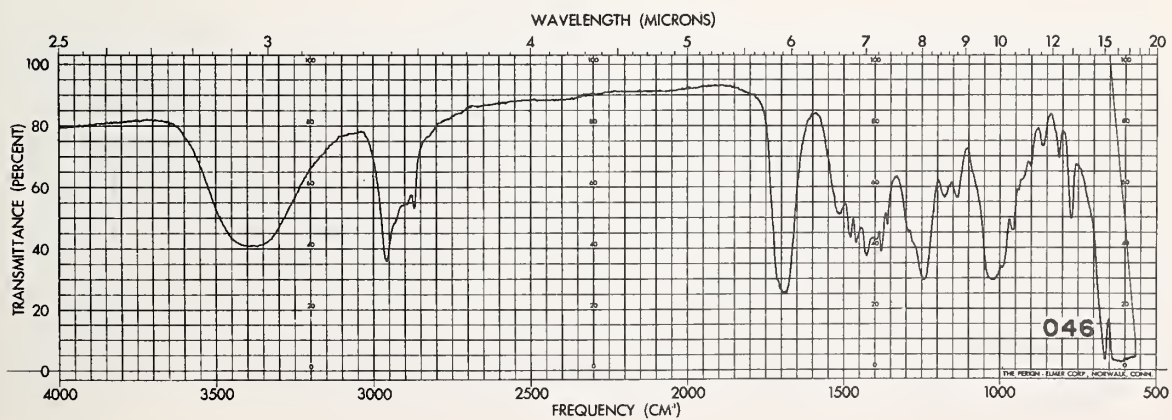
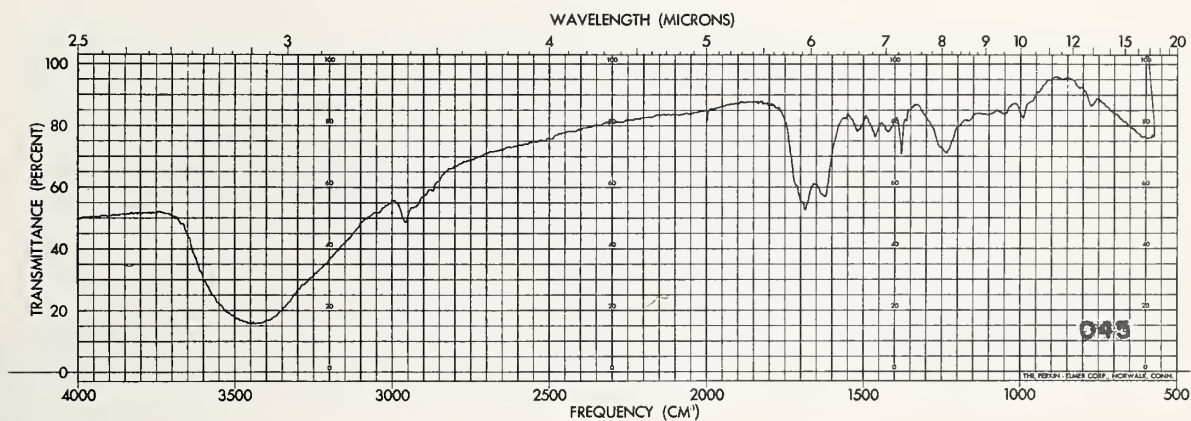
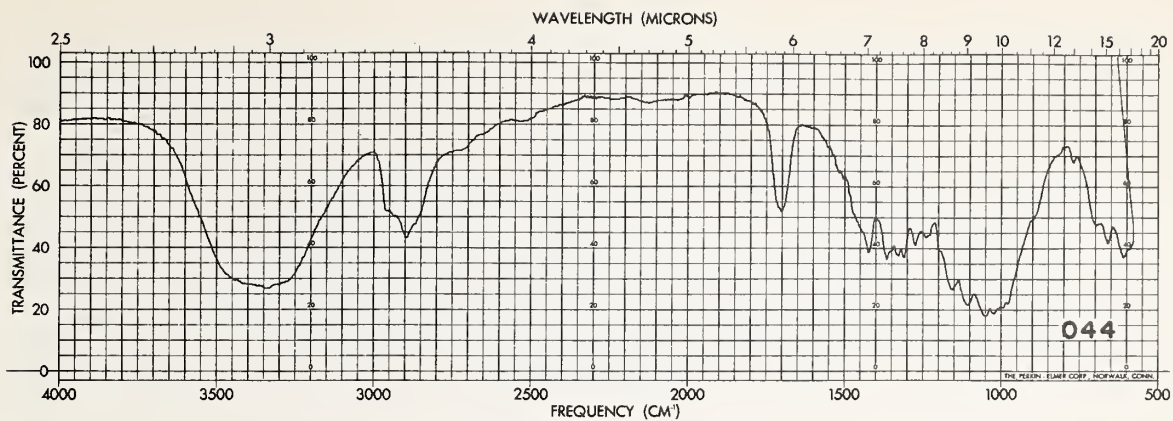


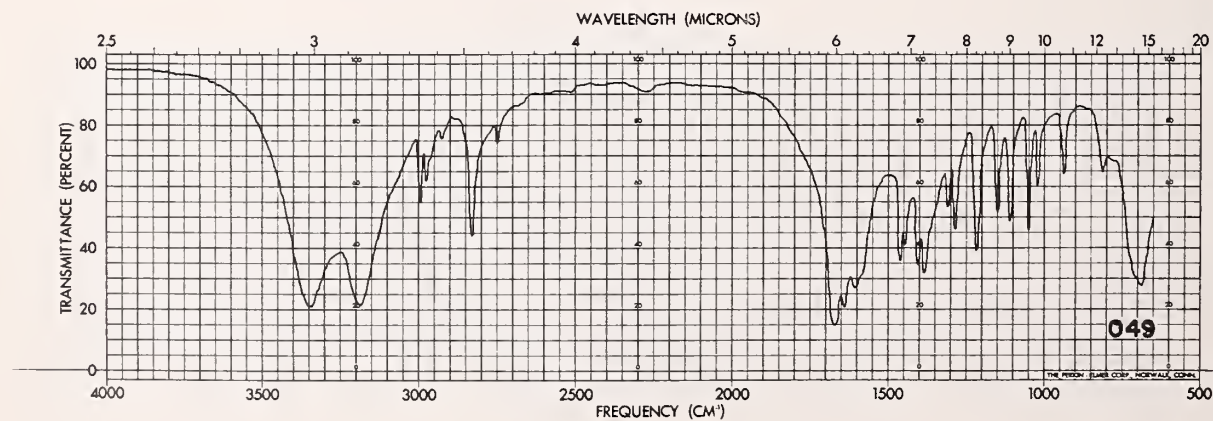
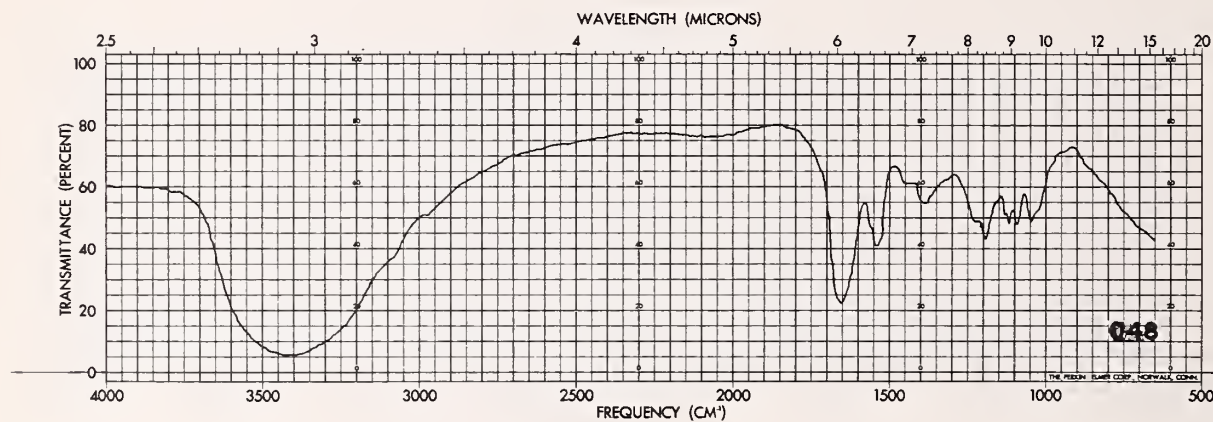
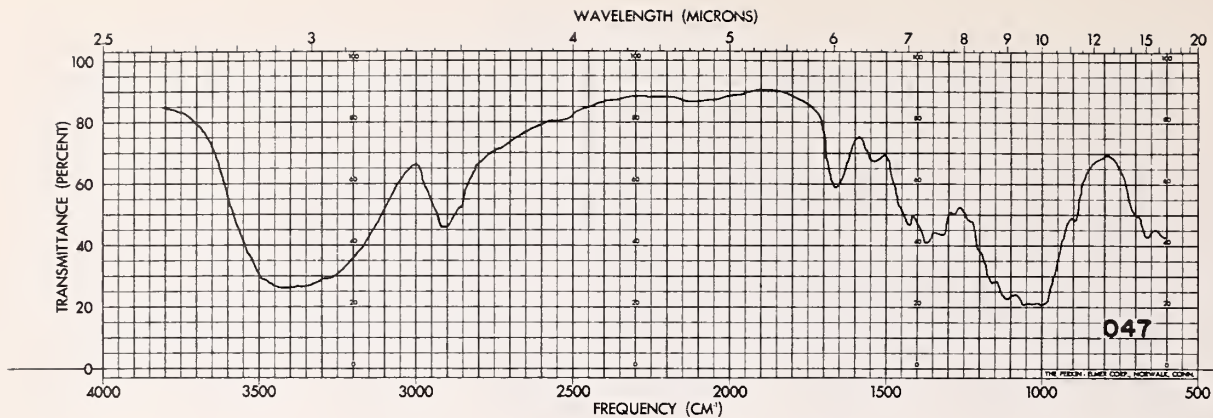


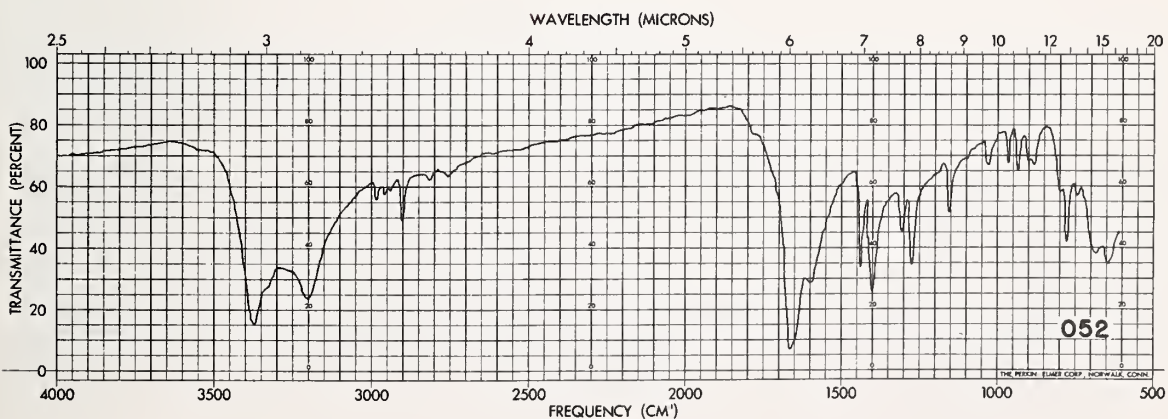
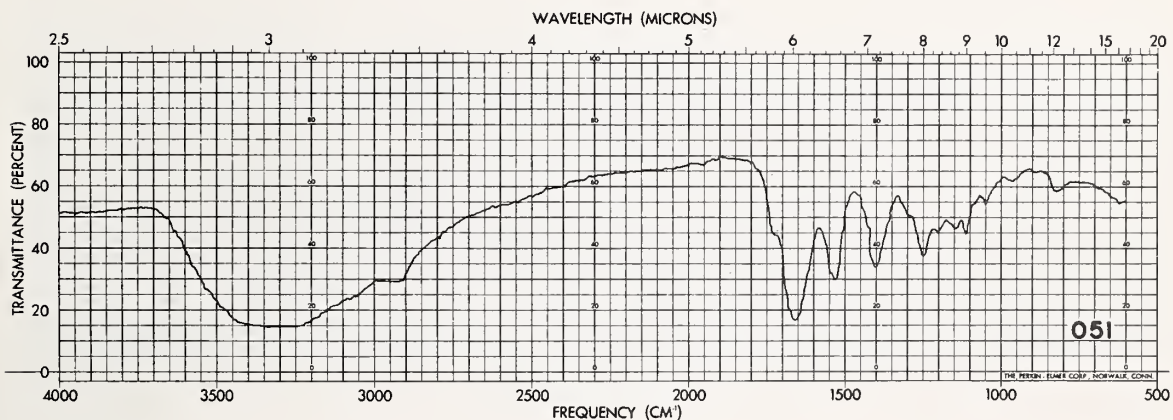
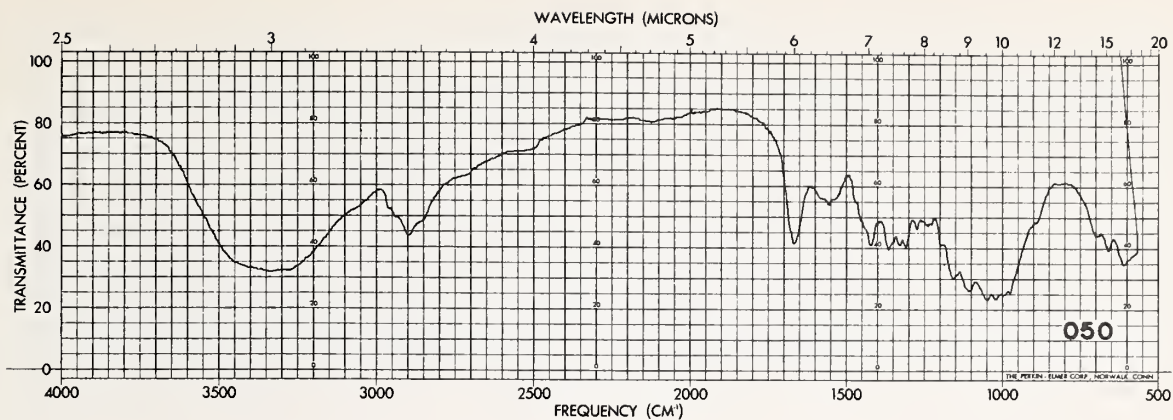


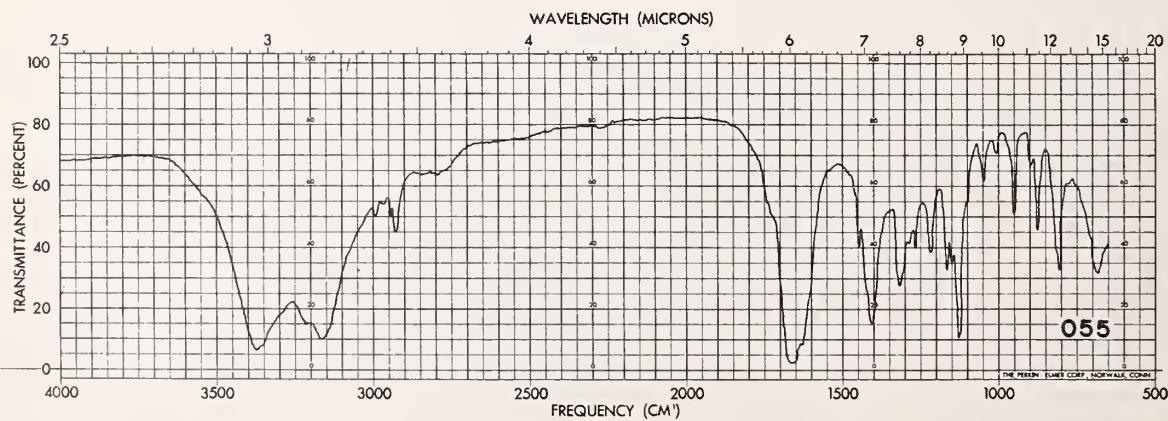
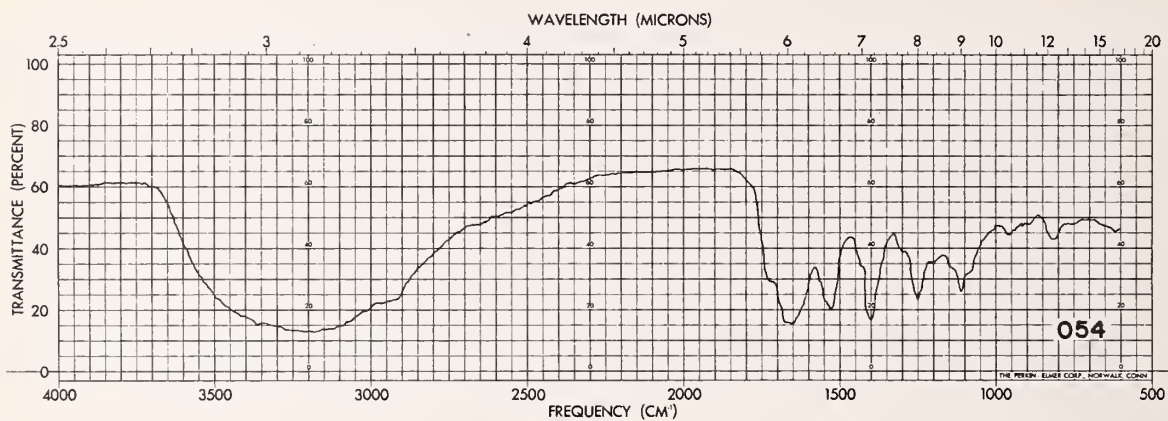
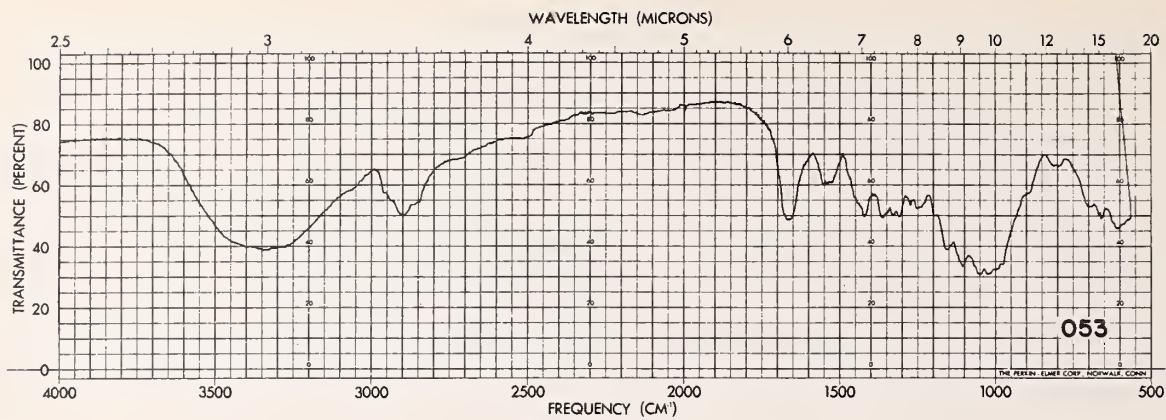


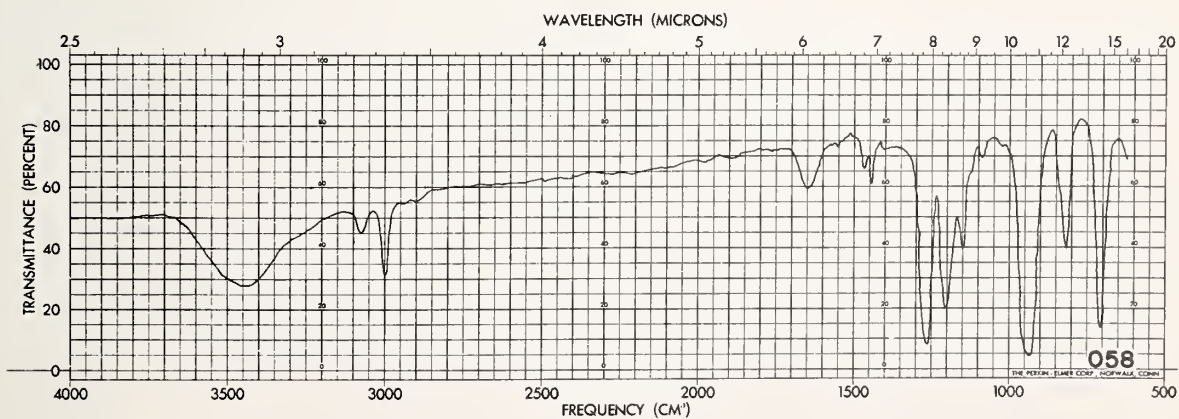
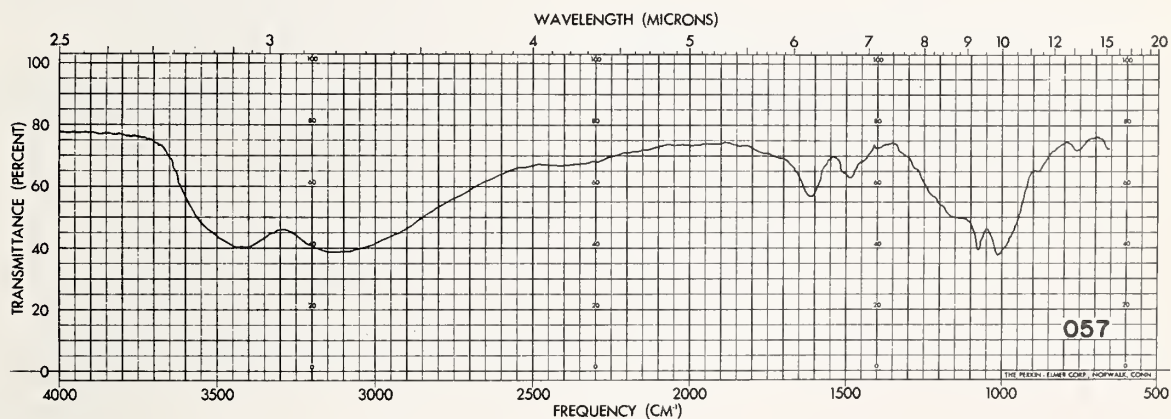
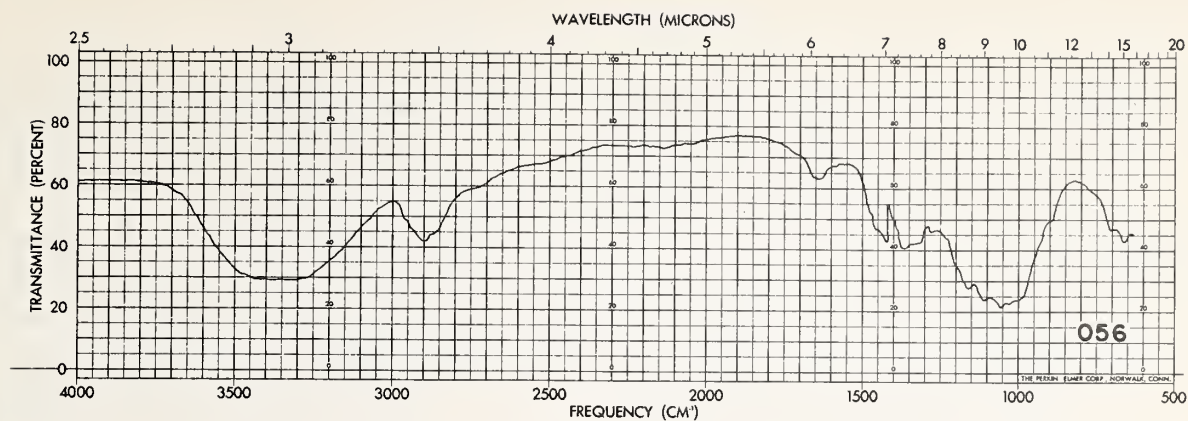












LITERATURE CITED

- (1) American Association of Textile Chemists and Colorists.
1973. Finishes in textiles: Identification. AATCC test method 94-1973. *In its* AATCC Technical Manual, vol. 49, pp. 65-77. Research Triangle Park, N.C.
- (2) Bellamy, L. J.
1954. The infrared spectra of complex molecules, pp. 203-233. John Wiley & Sons, New York.
- (3) Hummel, Dieter.
1962. Identification and analysis of surface-active agents by infrared and chemical methods. Vol. 2, Spectra. Interscience, Division of John Wiley & Sons, New York. (Translated by E. A. Wulkow.)
- (4) Infrared Spectroscopy Committee, Chicago Society for Paint Technology.
1969. Infrared spectroscopy, its use in the coatings industry. 465 pp. Federation of Societies for Paint Technology, Philadelphia.
- (5) Krammes, Ray, and Maresh, Charles.
1953. Identification of textile finishes. *Am. Dyest. Rep.* 42: 317-327.
- (6) McCall, E. R., Miles, S. H., and O'Connor, R. T.
1967. An analytical method for the identification of nitrogenous crosslinking reagents on cotton cellulose. *Am. Dyest. Rep.* 56: 35-39.
- (7) ——— Morris, N. M., Tripp, V. W., and O'Connor, R. T.
1970. Identifying softeners and fabric additives by infrared spectroscopy. *Text. Chem. Color.* 2: 105-116.
- (8) Miles, S. H., McCall, E. R., Tripp, V. W., and O'Connor, R. T.
1964. Infrared spectra of hydrolysis products of cottons reacted with typical nitrogenous crosslinking agents. *Am. Dyest. Rep.* 53: 440-444.
- (9) O'Connor, R. T., DuPré, Elsie, and McCall, E. R.
1957. Infrared spectrophotometric procedure for analysis of cellulose and modified cellulose. *Anal. Chem.* 29: 998-1005.
- (10) Skinkle, J. H.
1946. A systematic scheme of identification for organic finishing agents. *Am. Dyest. Rep.* 35: 449-452.

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